REFRACTORIES

By

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PREFACE TO THE FIRST EDITION

This book was written to fulfill the demand for a modern treatise on refractories. In order to keep it within a reasonable size it has been found necessary to deal mainly with the fundamental processes involved in the manufacture and use of refractories. Furthermore, the descriptions of the manufacturing processes have been confined to American practice. The important subject of the proper use of refractories in furnace design and construction has been omitted, since to do it justice a whole volume would be needed. On certain subjects it was found that a great deal of important information was lacking, and the attempt has been made in each case to indicate the direction in which research should be carried to provide the additional data needed for the understanding of the principles involved.

Although a portion of the material contained in this book has been taken from published data, a considerable amount of new material has been included. This has been obtained from the extensive work on refractories carried out in the laboratories of the Babcock & Wilcox Company. Unless otherwise stated, nearly all the experimental data in the book were derived from this source. In all cases the attempt has been made to indicate by the use of references, where additional information may be obtained on any particular subject.

Chapter XVI was prepared by Prof. J. L. Gillson of the Massachusetts Institute of Technology, whose experience in the examination of clays and ceramic products makes him especially well fitted to write on this subject. Chapter XVII was written by Prof. J. T. Norton of the Massachusetts Institute of Technology, who has been carrying on X-ray studies of crystals for a number of years. Chapter XVIII was prepared by Mr. J. B. Romer, chief chemist of the Babcock & Wilcox Company. Mr. Romer has had many years of experience in analyzing clays and ceramic products.

The author wishes to acknowledge the valuable assistance rendered in the preparation of this book by a large number of individuals connected with the refractories industry. I am particularly indebted to Mr. Isaac Harter, vice president of the Babcock & Wilcox Company; Prof. C. L. Norton, Prof. G. B. Wilkes, and Prof. C. E. Locke of the Massachusetts Institute of Technology; Mr. A. M. Kohler, Mr. J. E. Brinckerhoff, and Mr. Robert Richardson of the Babcock & Wilcox Company; and Mr. E. B. Powell of Stone & Webster, Inc.

A considerable number of industrial concerns connected with the refractories industry have cooperated most heartily in supplying up-to-date illustrations. Separate acknowledgment has been made in each case.

The numerous photomicrographs throughout the book are due to the painstaking work of C. L. Norton, Jr., who is carrying on research in ceramic petrography at the Massachusetts Institute of Technology, under a Babcock & Wilcox fellowship.

F. H. NORTON

CAMBRIDGE, MASS.
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Part I
INTRODUCTION

CHAPTER I

SCOPE OF THE REFRACTORIES INDUSTRY IN THE UNITED STATES

1. The Refractories Industry. Although the manufacture of refractories is not one of the largest industries, it is a particularly important one, as all processes using high temperatures are dependent upon it. The refractories industry in the United States has shown a rapid growth since the start of the century, as indicated by the production curve in Fig. 1.

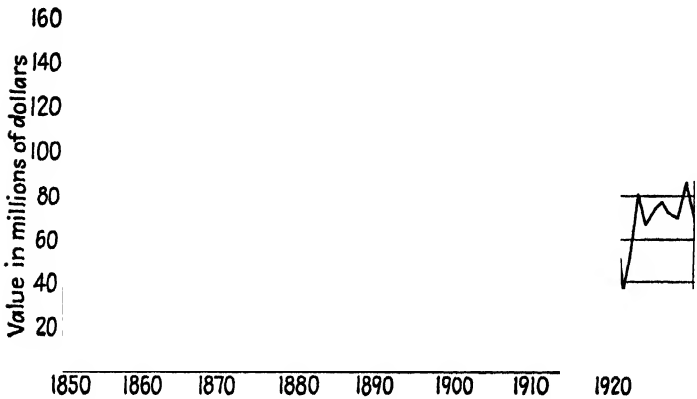

FIG. 1. Total value of refractories produced in the United States.

A more detailed picture of the refractories production in this country is shown in Tables 1 to 4, which give the quantities and values of various classes of refractories turned out each year. These tables indicate that many changes have occurred in refractory production especially if figures before and after the Second World War are compared. Fireclay and silica brick have about the same production volume, but they have increased in price about 50 per cent. High-alumina brick production also shows little volume change, but the price has nearly doubled. On the other hand, basic brick production has doubled both in volume and in price during the Second World War. The most striking change is the great increase in production volume of refractory cements (mortars, plastics, and castables), however, with only a small increase in price.

2. Refractories in Relation to Other Industries. Many industries are absolutely dependent upon refractories. For example, the power industry

uses great quantities in boiler furnaces, even though the tendency has been in the last few years to employ water-cooled walls in the larger units. The use of plastic chrome refractories to line the water walls has become a very general practice in powdered-coal and oil-fired boiler furnaces.

The iron and steel industry is vitally concerned with refractories, as evidenced by the large amount of research and development work in this field that is being carried out by the large companies. It may be said that not only the efficiency of the various units producing steel are vitally affected by the properties of the refractories but in some cases better qualities of steel could be produced if improved refractories were available.

In the nonferrous industry, refractories also play an essential part, both for withstanding high temperatures and for resisting various types of slag.

Refractories are also of vital importance to many other industries such as the kilns for ceramic production, glass furnaces, linings of rotary kilns for manufacture of Portland cement, incinerators, black-liquor furnaces, and even household oil-burner furnaces.

3. Recent Developments in the Industry. Since the publication of the previous edition, there have been some important changes in the manufacture and use of refractories.

While there still seem to be ample supplies of fireclay, the high-alumina clays such as diaspore and bauxite are becoming less available. Magnesite is being obtained from sea water and by chemical means from dolomite. A high-purity silica brick is being made from washed ganister, and the use of mullite and pure alumina brick is increasing. Rotary kilns are finding greater use in burning grog to high temperatures, and the firing temperature of bricks is gradually being increased, particularly for the super-duty brick, which is finding more extended markets. In general, laborsaving devices have come into greater use, especially the lift truck.

In the field of steam-power generation, water-cooled walls are more generally used, with plastics and castables replacing many of the fired shapes. The super-duty silica brick is finding use in the open-hearth roof, and trials of basic roofs are under way. The possible use of oxygen additions to combustion air makes refractories with higher use limits of great interest. Following European practice, a number of our blast furnaces are lined with carbon blocks or a rammed carbon mix, apparently with success. Pebble heaters have opened up a new field of high preheating for chemical processes and for very high temperature combustion.

A new and very active field of development is the refractories for jet-propulsion engines. Almost no refractory has as yet been used in these engines, but the possibilities are there. Then, too, the use of atomic energy will certainly require refractories of a very special kind. Neither of these fields will need any great volume of material, so the larger refractory

manufacturers have not been greatly interested as yet, and most of the work has been carried out by specialty manufacturers and government-sponsored research laboratories.

4. Future Trends in the Industry. It is to be expected that concentration methods will be used to a greater extent to produce more uniform raw materials, especially from high-alumina clays. On the other hand, we must not forget the inexhaustible deposits of pure sedimentary kaolin in the South, which will be called on to an increasing extent as the better fireclays are exhausted. The high-stability materials such as pure oxides, carbides, and nitrides will receive more attention as the need for higher temperatures becomes more acute. This will entail much research of a basic nature, which will later on be of the greatest value to the industry as a whole. The hot pressing of refractories will receive more attention, and developments are to be expected in plastics and castables.

SEARLE, A.B.: "The Chemistry and Physics of Clays and Other Ceramic Materials," D. Van Nostrand Company, Inc., New York, 1924.
MELLOR, J.W.: "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 6, "Silicates," Longmans, Green & Co., Inc., New York, 1926.
WASHBURN, E.W.: "International Critical Tables," McGraw-Hill Book Company, Inc., New York, 1927.
SOSMAN, R.B.: "The Properties of Silica," Reinhold Publishing Corporation, New York, 1927.
BRAGG, W.R.: "The Crystalline State," George Bell & Sons, Ltd., London, 1933.
HAUSER, E.A.: "Colloidal Phenomena," McGraw-Hill Book Company, Inc., New York, 1939.
EVANS, R.C.: "An Introduction to Crystal Chemistry," Cambridge University Press, London, 1939.
EITEL, W.: "Physikalische Chemie der Silikate," Voss, Leipzig, 1941.
PAULING, L.: "The Nature of the Chemical Bond," Cornell University Press, Ithaca, New York, 1944.

Books concerned with the measurement of high temperature are noted below.

BURGESS, G.K., and H. LE CHATELIER: "The Measurement of High Temperatures," John Wiley & Sons, Inc., New York, 1912.
GRIFFITHS, EZRA: "Methods of Measuring Temperatures," J. B. Lippincott Company, Philadelphia, 1926.
WOOD, W.P., and J.M. CORK: "Heat Measurements," McGraw-Hill Book Company, Inc., New York, 1927.
FISHENDEN, M., and O.A. SAUNDERS: "The Calculation of Heat Transmission," His Majesty's Stationery Office, London, 1932.
ANON.: "Temperature: Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York, 1940.
SOSMAN, R.B.: "Pyrometry of Solids and Surfaces," American Society for Metals, Cleveland, 1940.

The best available work on the history of refractories in the United States is

RIES, H., and H. LEIGHTON: "The History of the Clay Working Industry in the United States," John Wiley & Sons, Inc., New York, 1909.

There are a number of books dealing with the optical study of crystals, a few of which are noted below:

LARSEN, E.S.: "Microscopic Determination of the Non-opaque Minerals," Government Printing Office, Washington, D.C., 1921.
WINCHELL, N.H., and A.N. WINCHELL: "Elements of Optical Mineralogy," Vols. I, II, III, John Wiley & Sons, Inc., New York, 1927.
WINCHELL, A.N.: "Optic and Microscopic Characters of Artificial Minerals," University of Wisconsin, Studies in Science, Vol. 4, 1927.

2. Periodicals and Other Publications. A great many publications contain information on refractories, but only a few of them are devoted exclusively to refractories. The majority have only occasional articles dealing with this subject. From a scientific and technical point of view

the *Journal of the American Ceramic Society* and the *Transactions of the British Ceramic Society* are of the greatest importance. The periodicals in the following list have important or frequent articles on refractories:

American Ceramic Society, *Journal, Bulletin, Abstracts,* Columbus, Ohio.
American Refractories Institute, *Technical Bulletin,* Pittsburgh, Pennsylvania.
American Society for Testing Materials, *Proceedings,* Philadelphia, Pennsylvania.
Berichte der deutschen keramischen Gesellschaft, Berlin-Halensee, Germany.
Brick & Clay Record, Chicago, Illinois.
British Ceramic Society, *Transactions,* Stoke-on-Trent, England.
British Clayworker, London, England.
Ceramic Age, The Ceramic Publishing Co., Newark, New Jersey.
Ceramic Industry, Chicago, Illinois.
Ceramique, Paris (10e), France.
Glastechnische Berichte, Deutschen glastechnischen Gesellschaft, Frankfurt am Main, Germany.
Iron and Steel Institute, *Publications,* Grosvenor Gardens, London.
National Bureau of Standards, *Circulars, Scientific Papers, Technical News Bulletins, Technical Papers, Journal of Research,* Washington, D.C.
Ogneupory, Russia.
Ohio Ceramic Industries Association, *Bulletins,* Ohio State University, Columbus, Ohio.
Ohio State University Engineering Experiment Station, *Bulletins,* Ohio State University, Columbus, Ohio.
Refractories Journal, Sheffield, England.
Sprechsaal, Müller und Schmidt, Coburg, Germany.
U.S. Bureau of Mines, *Bulletins, Circulars, Mineral Resources, Reports of Investigations, Technical Papers,* Washington, D.C.
University of Illinois Engineering Experiment Station, *Bulletins,* University of Illinois, Urbana, Illinois.

3. Bibliographies. There are a number of excellent bibliographies covering the complete ceramic field as well as limited portions of it pertaining directly to refractories. The following bibliographies cover the complete field of ceramics quite thoroughly up to the time of their publication. M. L. Solon gives us critical abstracts of most of the books and also an excellent classification. However, he writes mainly from the point of view of the artist, and the number of references of value on modern refractories is limited.

BRANNER, J.C.: "A Bibliography of Clays and the Ceramic Arts," American Ceramic Society, Columbus, Ohio, 1906. Covers whole ceramic field up to 1906.

SOLON, M.L.: "A Bibliography on Ceramic Literature," Charles Griffin & Co., Ltd., London, 1910. Critical abstracts are given of most of the books. Well classified.

In the following list are included a number of up-to-date bibliographies dealing with special refractory divisions, which will be found of more direct value than the preceding list.

MARDEN, J.W., and M.N. RICH: Bibliography on Zirconium and Its Compounds, *U.S. Bur. Mines, Bull.* 186, 1921.

4. Abstracts. The most complete abstracts of the literature on refractories are found in the *Journal of the American Ceramic Society* and the *Transactions of the British Ceramic Society.* In *Science Abstracts* and *Chemical Abstracts* will be found quite a few references to the more scientific and technical phases of this subject.

Throughout this book at the end of each chapter have been placed the more important references and publications dealing with the subject of that particular chapter. The selection of these references was somewhat difficult because of the tremendous mass of available material. However, the choice was guided by the amount of original data included in the reference and its accessibility in the average library. Also the more recent articles were considered in place of the early ones except where an early article was a particularly valuable or an original contribution to the subject.

CHAPTER III

HISTORY OF REFRACTORY DEVELOPMENT IN THE UNITED STATES

The early history of refractories in the United States is shrouded in considerable obscurity. A number of references are given here that throw new light on the subject, but a tremendous field still remains to be explored. A few months spent in examining old publications and records of Boston, Baltimore, Philadelphia, and parts of New Jersey would certainly yield valuable information. A little archaeological study around the sites of old furnaces, kilns, and plants would surely produce specimens of the old refractories used.

FIG. 2. An old iron furnace standing in Bennington, Vermont.

1. Furnace Stone. Undoubtedly the earliest type of refractory used in this country was mica schist or siliceous rock. All the early iron furnaces or forges were constructed mainly of this material. Thus we must study the early history of the iron industry. Fortunately this is quite well known, for an iron furnace was much more likely to be a subject of comment than a brickyard. The first furnaces were built in Virginia, but it is quite certain that they were never completed. The first successful furnace was built in 1645 at Saugus, Massachusetts, and the next year another was operated at

Braintree. They were probably made from local stone, although there are no very satisfactory deposits in this region. The building of furnaces and forges spread rapidly in the next hundred years, and considerable stone must have been quarried. Samuel Robinson[1]* in 1825 states that furnace stone was quarried near Providence, Rhode Island, for forty or fifty years and carried long distances in wagons for use in furnace hearths. There were probably other famous quarries at this time.

Stone was used for the building of furnaces and forges late into the nineteenth century because of the greater cost of firebrick. Even now, stone is used for lining Bessemer converters. A number of the old stone or stone and brick furnaces are still standing in various parts of the country. Two interesting ones stand on Furnace Brook in Bennington, Vermont, one of which is shown in Fig. 2.

Records[20] show that sandstone was used for the walls of kilns burning refractories. Probably many of the early glass furnaces were built of stone. In fact Robert Hewes of the Temple Glass Company, Temple, New Hampshire,[7] states in a letter dated 1781: "I shall have to send sixty miles for stones to build my melting furnace, which will take eight teams." It is believed that these stones came from Uxbridge, Massachusetts, which is about sixty miles from Temple. Samples from the old furnaces confirm this.

2. Glass Pots and Crucibles. Probably the first clay refractories used in this country were glass pots. J. B. Felt[5] in his "Annals of Salem" in 1827 mentions a glass factory in Salem, Massachusetts, in 1638 and again as producing in 1641. The only other information I have been able to obtain is the names of John and Ananias Conklin as glass blowers. All else seems to be lost in the obscurity of time. We may be sure, however, that glass pots were used. They were probably made from English or German clays as were all the early glass refractories.

A century later, the Wister glassworks were started in New Jersey. Gross Almerode or Klingenberg clay was used for the pots at first, but later New Jersey or Maryland clays were probably used to some extent. J. C. Booth[4] in 1841 states that a white, highly plastic clay was wrought only in one place, on the Delaware shore below New Castle, and exported for crucibles and glass pots. The clay had been wrought for manufacturing purposes for some forty years. Porcelain crucibles were made of kaolin from New Milford, Connecticut, by a goldsmith in about 1807.

A number of other early glass plants were operated in this country, mainly by Germans. We have the Germantown factory (Braintree, Mas-

* Numbers thus set in parentheses refer to the bibliographies appearing at the end of each chapter.

sachusetts) and the factory of Baron Steigel in 1763, as well as a number of others. German pot clays were probably extensively used as they are even now. In fact, J. F. Amelung, who started a glassworks at Frederick, Maryland, in 1784, brought over pot makers and built a pot works in conjunction with his plant.

A note in the Gaffield Collection at the Massachusetts Institute of Technology library states that the Boston Crown Glass Company, which for a number of years had been using imported clays for pots, attempted between 1810 and 1812 to replace them with domestic (probably New Jersey) clays. The attempt was not successful.

A recipe book of the Boston Glass Mfg. Co. in the Boston Athenaeum Library has an item dated 1791 stating that 200 lumps of clay were received from Amsterdam, undoubtedly for making pots. Another item lists fuel for keeping the glass pots (green) from freezing.

The manufacture of glass pots as an industry separate from the glass plants was started in 1860 by Thomas Coffin in Pittsburgh.[12] In 1879, the Pittsburgh Clay Pot Company was organized, and after this many other concerns started in Pennsylvania and Ohio.

3. Lime. Lime, often made from shells gathered on the shore, was used in forge walls from very early times. There are references to a number of early lime kilns.

4. Fireclay Bricks. We are still in doubt as to the location of the first American firebrick manufacturer. It may have been New Jersey, Boston, or Baltimore.

New England. Owing to the early development of iron and glass manufacture here, it is to be expected that firebrick would be needed at an early date. Stourbridge firebricks (English) are known to have been imported to some extent, but bricks were also made from New Jersey clay. The recipe book of the Boston Glass Mfg. Co. states that in 1790, two helpers were paid to make furnace tile and, in 1791, two men were paid for burning brick for the glass furnace. In 1793, an item lists the payment of expenses for a man to go to New York to procure clay from South Amboy. This is undoubtedly the earliest direct reference to the manufacture of firebrick from native clay. According to Professor Rogers,[8] Mr. G. W. Price of New Brunswick, New Jersey, stated that his father carried a vessel load of fireclay from Woodbridge to Boston in 1816 for use in making firebricks. It was thought to be the first shipment for this use. An advertisement in the *Boston Commercial Gazette* of July 6, 1818, by the New England Glass Company, read, "Also—Fire Brick Clay, raw and prepared, constantly for sale." This would seem to indicate that firebricks were then being made in Boston. In 1820, Jacob Felt of Boston bought 50 tons of clay of Jere-

miah Dully, and this was afterward sent regularly from Amboy. Firebricks were made in Boston at this time.

The following advertisement appeared in the *Boston Commercial Gazette* of Mar. 5, 1827. "_____fire bricks made to all dimensions. For sale by Deming Jarves, No. 88 Water St." (New England Glass Bottle Works.) This probably explains where at least part of the New Jersey clay was used.

In 1835, a patent was taken out by Joseph Putnam of Salem for firebricks and stove linings. We do not know whether or not he manufactured, but it is doubtful if he would have applied for a patent for this type of article without having previously made it. As early as 1829, L. Hine used the kaolin of New Milford, Connecticut, for firebricks and furnace linings.[3] He evidently had a considerable business, as $6,000 per year is mentioned as the value of his product and six workmen were employed. The bricks sold for two-thirds the price of the Stourbridge firebricks and were considered nearly as good.

In 1839, Hiram Harwood of Bennington, Vermont, records in his diary,[18] "Visited works of Judge L. Norton—large low buildings in forwardness for drying newly invented fire bricks—erected N. old works." This business apparently prospered in the next few years and was carried on by Norton and Fenton. It is quite possible that the manufacture of these bricks was started from information obtained from the New Milford enterprise. We are fortunate in having an accurate account of the manufacture of these early bricks by Norton and Fenton. C. B. Adams, state geologist of Vermont, in his first *Annual Report* (1845), page 52, states:

> For firebrick, the kaolin is made into paste with water, from which bricks are formed and burnt. These bricks, retaining the whiteness of the kaolin, and becoming very hard, are called "clay bricks." They are next broken up by a mill and sifted, so as to be of the coarseness of fine gravel. This is mixed with unburnt kaolin and arenaceous quartz, pressed in moulds of the required form and size, and burnt in the same manner as before. These firebricks are very white and hard, and when fractured shew their composition of broken claybrick and kaolin.

C. W. Fenton, in a letter to Mr. Adams at this time, gives more particulars:

> The character of our fire-bricks is also well known. They are a composition of materials which we find here, consisting of arenaceous quartz and kaolin. Being very pure, they make a good fire-brick, which will stand longer in a strong heat than any other brick known. They are used for blast furnace hearth, and in many places, where no other fire-bricks will endure.

The value of pottery and firebrick produced then was stated as $20,000 per year.

In 1841 (Feb. 27), the following advertisement appeared in the *State Banner* of Bennington, Vermont:

Bennington
Stoneware Factory
Julius Norton
Manufactures and keeps constantly for sale
. . . . . .
Also *Patent Fire Brick*
(the best in the world) at $50 per thousand

These kaolin bricks were made in Bennington as late as 1855 or 1856 and had a very general sale as a good firebrick. But owing to the lack of coal and the need of twice burning the highly shrinkable kaolin, they could not long compete in cost with bricks of New Jersey and Pennsylvania.

It is also stated that firebrick of kaolin, New Jersey fireclay, crushed brick, and sandstone from Willsboro, New York, were made at Monkton, Vermont, in 1846. These bricks were undoubtedly used in the many charcoal iron furnaces operating in this region, although a large part of the lining was quartzite or mica schist. A reddish firebrick taken from an old furnace standing on Furnace Brook in Bennington, Vermont, fulfills this description quite well. I was also fortunate in finding at the site of the United States Pottery in Bennington a white brick made of coarse calcined grog bonded with kaolin. This brick is marked:

Fire Brick Co's.
No. 1
Bennington, Vt.

Considerable space is given to these early kaolin bricks, because we have a fairly complete account of their manufacture and because they are the first to utilize successfully the pure and refractory but high-shrinking kaolin by the method of double burning. For their time, they were really remarkable bricks and have scarcely been mentioned in histories of refractories.

Firebricks and retorts were probably being made in Boston regularly before 1850. In 1864, the Boston Fire Brick and Clay Retort Manufacturing Company was making bricks and retorts on the site of the present South Station. New Jersey fireclay was brought to their own dock. For some years at about this time, the Morton Fire Brick Plant on K Street at South Boston was in operation. Apparently no firebrick has been made in Boston since 1895.

From the beginning of the nineteenth century, a number of stoneware potteries were operating in New England. In every case, firebrick must have been used in their kilns. It is reasonable to suppose that the bricks were made from stoneware clay, all of which at that time came from New Jersey.

17359

The manufacture of stove linings and firebricks has been carried on at Taunton, Massachusetts, for many years. Now Pennsylvania clays are mainly used.

New Jersey. A stoneware pottery was operated by Coxe at Burlington, New Jersey, in 1684. He probably used English firebrick for his kilns, but some local clay may have been used.

Professor Rogers[8] states that New Jersey clays were used for making firebricks soon after 1812. We need not necessarily assume, as many have, that the bricks were made in New Jersey. The clay may have been taken to Boston or Baltimore. In 1825, a firebrick plant (Salamanda Works) was started at Woodbridge, New Jersey. In 1836, John R. Watson established a factory for making firebricks at Perth Amboy. From 1845 to 1865, a number of plants were started in the Woodbridge district, and most of them are still operating. Sayer and Fisher, Henry Maurer & Son, and Valentine & Bro. are well-known firebrick manufacturers at the present day.

Delaware and Maryland. In a report[2] on the state of Maryland, published in 1834, occurs a most significant statement:

> Fire brick so far exclusively made in the United States at Baltimore, has been pronounced by competent judges after repeated trials, to be fully equal, if not superior to the far-famed Stourbridge brick of the same nature.

Later it stated that these bricks were used in iron furnaces to replace silica stone.

We may judge from this statement that a high-grade firebrick of the "same nature" as the well-known Stourbridge firebrick was an established industry in Baltimore at this time. The reference to repeated trials would indicate its use for a considerable number of years previous. The statement that firebricks were made only in Baltimore at this time is perhaps founded on lack of knowledge of the industry in New Jersey and Boston but more probably refers to a time some years prior to this date when the Baltimore industry was started. Further investigation is greatly needed on this point.

As previously mentioned,[4] considerable white refractory clay was mined in Delaware mainly for crucible and glass pots, but some may well have served for bricks.

In 1837, the famous Mt. Savage fireclay was discovered, and the Union Mining Company soon began operations here.

Florida. Ries[12] states that records show a shipment of firebrick from Florida to New Orleans in 1827. No more is known of it.

Ohio. According to Stout,[20] firebricks were first made in Ohio during 1841 by Andrew Russell near East Liverpool. They were produced there continuously until about 1900 by Russell and later by N. U. Walker. The

clay mined behind the plant was plastic and of medium refractoriness. In 1852, G. and M. Meyers started a firebrick plant near Toronto. A plastic, lower Kittanning clay was used.

The manufacture of firebricks from flint clay was begun during 1863 in Scioto County by Reese Thomas. This brick was a high-grade product, made in updraft kilns with sandstone walls.

During 1866, the Diamond Fire Brick Company was opened in Akron by J. P. Alexander. At about the same time, a three-kiln plant was built at Dover. The Federal Clay Products Company and a number of other plants started about 1872 in this district. J. R. Thomas founded the Niles Fire Brick Company at Niles in 1872.

The Oak Hill Fire Brick Company and Aetna Fire Brick Company started in the Oak Hill district about 1873. Other plants were opened here later.

Pennsylvania. It has generally been believed that the first firebricks were made in Pennsylvania about 1836 at Queens Run. However, the following advertising card[10] would indicate that they were made in Philadelphia before 1832.

American China Manufactury
S. W. Corner of Schuylkill Sixth & Chestnut Sts.,
or at the Depository
Where is constantly kept on hand,.. ....

also offered for sale
Fire-brick & Tile
Of a superior quality, manufactured in part from the materials of which china is composed.—These have been proved, by competent judges, to be equal to the best Stourbridge brick.

Eight years later the following advertisement[10] appeared.

Abraham Miller
has removed his manufactory
From Zane Street to James, near Broad Street,
Spring Garden
where his works are now in full operation, conducted by his late Foreman, Mr. J. C Boulter.

A large Assortment of Portable Furnaces, Stove Cylinders, Fire Bricks and Slabs,
.....
.....
Philad'a December 22d 1840.

In 1842, James Glover started the manufacture of refractories at Bolivar. The clay is of good quality, and refractories are still made there. In

1845, Kier Brothers started to manufacture at Salina. In 1859, Soisson and Company began manufacturing at Connellsville; and in 1865, the Star Fire Brick Works were built at Pittsburgh.

After this, so many firebrick plants were opened in the state that it assumed the leading position in the manufacture of refractories. The factors contributing to this great development were the excellent deposits of clay, especially flint clay; the abundance of coal; and the ease of distribution.

Missouri. In the year 1846, the excellent clay deposits of the St. Louis district were opened up. In 1855, the Christy Fire Clay Company was started; and in 1855, both the Evans and Howard and the Laclede Fire Brick Company followed. The St. Louis district was one of the largest producing centers at this time.

Kentucky. This district was not opened up until about 1871, when fireclay from Lewis County was sent to Cincinnati. In 1884, the clays at Amanda Furnace and Bellport Furnace were worked. Two years later the Ashland Fire Brick Company was started at Ashland.

West Virginia. Firebricks were not produced in this state until 1876, when the clays of Marion County were worked.

Colorado. The first firebricks made in this state were manufactured at Golden during 1866. Later clay deposits were opened up at Pueblo and Cañon City and now have a good reputation in the West.

The West Coast. Refractory manufacture was rather late in developing here, but recently many excellent refractories are being made in both California and Washington.

5. Silica Refractories. Probably the first silica bricks made in the United States were manufactured by J. P. Alexander of Akron, Ohio, about 1866, but a patent was granted to Thomas James[6] in 1858 for a lime-bonded silica brick, and he may have manufactured before Alexander. Of course, in England lime-bonded silica brick was made even before this.[23] J. R. Thomas made silica brick for the steel industry at Niles, Ohio, about 1872. He used quartz pebbles and a Sharon conglomerate and called the bricks "Dinas Silica," as they were similar to the European brick of that name. A. Hall of Perth Amboy made some silica bricks in 1875, but apparently there was no great demand for them. The modern silica brick of lime-bonded ganister is a more recent development. In the year 1899, the first silica-brick plant was started at Mt. Union, which later became a great center. Silica bricks were made later in the Chicago district.[21]

6. Chrome Refractories. Chromite, mainly in the form of bricks, began to be used by the steel manufacturers about 1896, chiefly as a neutral zone between the acid and basic courses. Only a few firms have been manufacturing chrome bricks.

7. Magnesite Refractories. Magnesite as a steel-furnace lining was suggested in Europe as early as 1860 but did not come into regular use until 1880, when it was found that the Austrian material could be fritted down into a good bottom. Styrian magnesite was imported into this country in 1885 and was used by the Otis Steel Company in the first open-hearth steel plant in the United States. However, it was not a commercial success. In 1888, magnesite was used successfully by Carnegie, Phipps & Co. at Homestead. From this time, the use of magnesite increased rapidly because the general advantages of the basic process over the acid process became evident to all.

In the year 1898, 16,000 tons of Austrian dead-burned grain were imported. Bricks were at first imported, but later they were made in this country by a few companies.

8. High-alumina Refractories. The first bauxite discovered in the United States was found near Rome, Georgia, during 1888.[14] The Arkansas bauxite deposits were discovered in 1891. The production from the latter source increased rapidly until now it supplies a considerable part of the domestic demand. Coastal bauxite of Georgia was discovered and described in 1909. A number of small deposits are now being worked.

Missouri diaspore was recognized in 1917 as a source of material for super refractories. This discovery has made Missouri one of the most important producing states.

The importation of gibbsite from Dutch Guiana in the last few years has supplied a very high-grade material to the manufacturers of refractories.

The deposits of sedimentary kaolin on the southern coastal plain have been known from the time of the first settlers. The remarkable beds form probably the largest supply of uniform and pure high-grade clay in the world. The suitability of kaolin for refractories was known as early as 1837 in Bennington, but the southern kaolin is of a purer grade and possesses a high vitrifying point and a very large shrinkage. These properties for many years have prevented its use in a refractory. During the last twenty-five years, however, it has been possible to manufacture a successful refractory out of this pure kaolin.

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Part II
MANUFACTURE

CHAPTER IV

REFRACTORY RAW MATERIALS

1. Clays. *Definitions.* It seems impossible to give a definition for a clay that is inclusive and yet free from exceptions. Many of the characteristics generally associated with clays, such as plasticity, water of hydration, and plate structure, are found in other materials. The best that can be done is to define a clay broadly as a hydrated earthy material, containing a considerable portion of alumina or silica and showing the property of plasticity.

More specifically the following definitions have been proposed by the Committee on Geological Surveys of the American Ceramic Society.[197]

Bauxitic Clay: A clay consisting of a mixture of bauxitic minerals, such as gibbsite and diaspore, with clay minerals, the former constituting not over 50 per cent of the total. (The opposite of this would be an argillaceous bauxite.)

Burley Clay: A clay containing burls, oölites, or nodules, which may be high in alumina or iron oxide. As used in Missouri, it refers to a diaspore-bearing clay usually averaging 45 to 65 per cent Al_2O_3.

Diaspore Clay: A clay usually containing over 60 per cent alumina with the mineral diaspore often in shotlike particles, or "oölites." There may be some gibbsite or cliachite present.

Fireclay: A clay either of sedimentary or residual character that has a P.C.E. of not less than cone 19. It may vary in its plasticity or other physical properties; and while it often fires to a buff color, it does not necessarily do so. It is recommended that clays with a P.C.E. from 19 to 26, inclusive, be called "low heat-duty fireclays" and that fireclays with a P.C.E. of cone 27 or higher be designated "refractory."

The terms "Nos. 1, 2, and 3 fireclay" as sometimes used do not always refer to the same degree of fusibility.

While some fireclays are found underlying coal beds, many show no association with coal; in fact, some clays underlying coal beds do not conform to the description given.

Flint Clay: A clay, usually refractory and hard, with a dense structure and conchoidal fracture. It is difficult to slake and has little plasticity under usual working conditions.

Kaolin: A white-firing clay which, in its beneficiated condition, is made up chiefly of minerals of the kaolinite type. Two types of kaolin may be recognized as follows:

1. Residual kaolin: A kaolin found in the place where it is formed by rock weathering.

2. Sedimentary kaolin: A kaolin that has been transported from its place of origin. Sedimentary kaolins show more pronounced colloidal properties than residual kaolins.

The distinction between kaolin and fireclay is not particularly clear, as both contain almost wholly the mineral kaolinite. In this book, *kaolin* will be used for white-burning clays, and *fireclay* for buff-burning clays. Also, bauxite and bauxitic clays will be reserved for those whose gibbsite content predominates over the diaspore content.

FIG. 3. An electron microscope photograph of kaolinite crystals, the larger ones being just over a micron in diameter. (*Courtesy of the Georgia Kaolin Company.*)

The Nature of Clay. During the last twenty years, tremendous progress has been made in painting a true picture of the nature of clay. At present, although parts of the picture are indistinct, the framework is there and many details are clear. It is now certain that the clay—even to its finest particles—is composed of fragments of definite minerals. Because of the minute size of these crystals, their identification and description are particularly difficult. Great credit is due to mineralogists such as Ross, Kerr, Grim, Hendricks, and Gruner in this country; Marshall in England; and Endell and Nagelschmidt in Germany. Although additional clay minerals will undoubtedly be identified in the future, the classification given in Table 6 seems to be the most logical arrangement at present. It is known that these minerals occur in the clay over a wide range of sizes between 100 and 0.01 μ, but a large majority of the clay particles range

between 0.2 and 10 μ. No general evidence indicates that the finer fraction or colloidal portion (below 0.5 μ) is any different, except in size, from the coarser particles. The particles in a clay are mainly platy, although we cannot, at present, measure the actual shape of the extremely small particles. Fig. 3, showing submicroscopic kaolinite crystals, gives an idea of the particles in a sedimentary kaolin.

The clay particles have attached to their surfaces various adsorbed ions, such as Ca, Na or SO_3, that markedly affect their physical properties. With the clay minerals is often associated organic matter such as lignite and humus, which may act as protective colloids and influence the physical properties of the clay. Most clays also contain impurities, often of large grain size, such as quartz, mica, feldspar, and other nonplastic minerals. Also the clay minerals themselves can have iron and other metallic atoms in the crystal lattice.

The Origin of Clay. Clay is always an altered product derived by weathering or hydrothermal action from rocks rich in feldspar. There is still no agreement among geologists as to the exact mechanism of clay formation or why various clay minerals are apparently obtained from the same parent rock. In most cases, the action is principally one of removal of the alkalies and decrease of the silica, the former being removed as soluble salts and the latter as colloidal silica. When silica removal is carried to the end point, as a result of the high permeability of the mass to the percolation of ground water, gibbsite or diaspore is the result. We are not sure whether a step-by-step process occurs or the reaction goes directly from the feldspar to an end point.

Clay minerals have been produced in the laboratory[80] under certain conditions of temperature and acidity from feldspars, the reaction taking place most rapidly at about 300°C. It would have seemed curious a few years ago that under identical reaction conditions, the end product of potash feldspar, for example, is sericite whereas from calcium feldspar, montmorillonite is produced; *i.e.*, the cation in the original rock, the original atomic arrangement, or both together seem to have some control over the type of end product. Geologists now are beginning to believe that in all metamorphic changes, there is some relation between the atomic structure of the original material and its product.

Clays found in the same location as the parent rock from which they were formed are called "residual clays." Such clays usually contain rock fragments and thus require washing, for which reason they are not used to any great extent in refractories. The primary kaolins of North Carolina are a good example of a residual clay.

Transported clays are sediments deposited in lakes, swamps, or the ocean. They may be considerably altered during and after transportation. The sedimentary kaolins of Georgia and most fireclays are examples.

The classification of clays according to origin in Table 5, as suggested by Stout, will be helpful in understanding the process of clay formation.

The excellent chart by Chelikowsky[29] gives a picture of geologic distribution of fireclays in the United States, and the maps by Ries[42] are complete and up to date.

TABLE 5. CLASSIFICATION OF CLAYS AS TO ORIGIN*

Residual matter	No movement during formation	Products of ordinary weathering	From crystalline rocks	Impure residual clay
				Primary kaolin
			From sedimentary rocks	Impure residual clay
				Kaolinitic clay
		Same as above with additional chemical action	From crystalline rocks	Bauxite
			From sedimentary rocks	Bauxite
				Diaspore
Transported matter	Deposited in still water, little or no current action, seas, lakes, bogs, etc.	Products of ordinary weathering		Argillaceous shale
				Argillaceous silt
		Same as above with additional intensive chemical action		Sedimentary kaolin
				Ball clay
				Some bauxite
				Coal-formation clay
				Diaspore
	Deposited by slowly moving waters, streams, estuaries, etc.	Products of grinding with some weathering		Siliceous shale
				Siliceous silt
	Deposited by glacial action	Products of abrasion with slight weathering		Glacial clay or till
	Deposited by winds	Products of abrasion with slight weathering		Loess

* Lecture on Clays by W. Stout, at Massachusetts Institute of Technology, 1937.

Clay Minerals. The clay minerals may be divided into definite types; but since various degrees of isomorphism can occur, there is a variability in composition that makes classification and identification difficult. The grouping indicated in Table 6 gives a reasonable picture of their relationship based on our present knowledge. The atomic arrangement shown in Fig. 4 is a probable one, but only in the case of dickite is it uni-

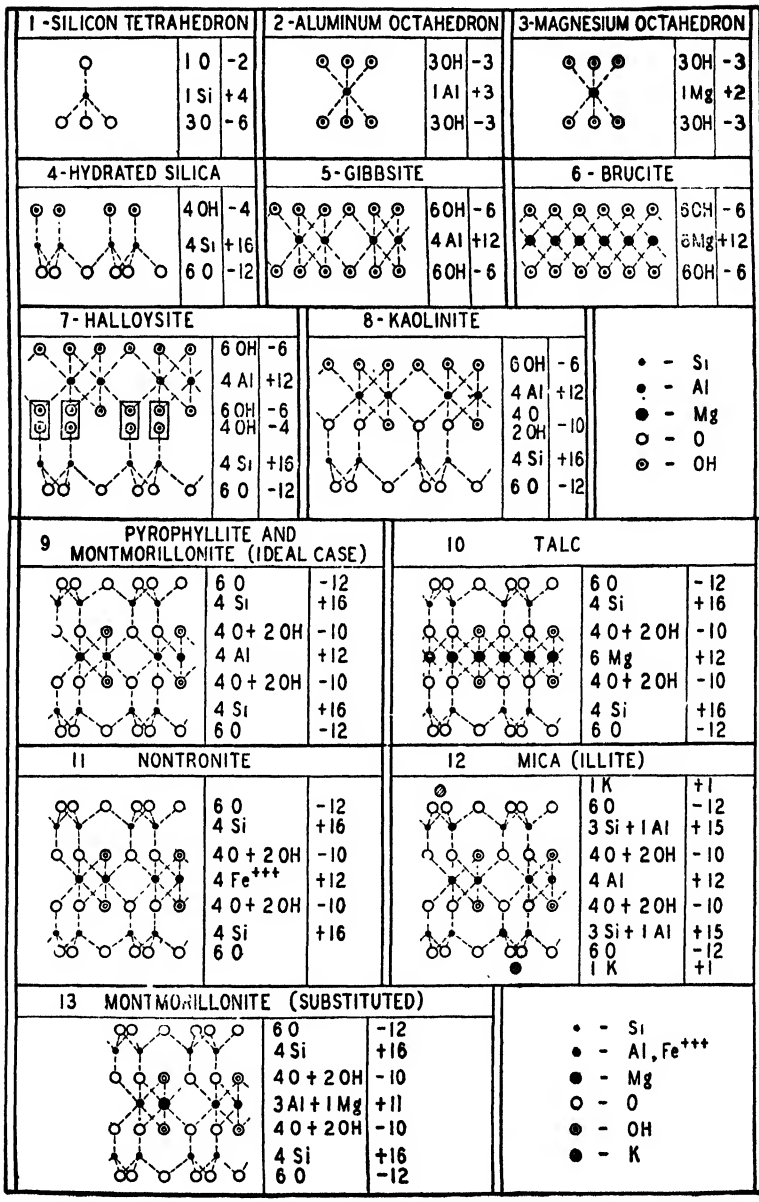


FIG. 4. Structural data of the clay minerals. First column is schematic drawings (not to scale) of the atoms in a unit cell projected into one plane. Second column gives number and type of atoms in each lattice plane and third column gives the corresponding valence charges. Where (+) and (−) charges are equal, lattice is neutral; where unequal, the charge is equal to the algebraic difference. (*From E. A. Hauser, J. Am. Ceram. Soc.*)

TABLE 6. THE CLAY MINERALS

Kaolinite group	Montmorillonite group	Micaceous group	Aluminous group
Kaolinite, $Al_2(Si_2O_5)(OH)_4$	Pyrophyllite,* $Al_2Si_4O_{10}(OH)_2$ Talc,* $Mg_3Si_4O_{10}(OH)_2$	Muscovite,* $Al_4K_2(Si_6Al_2)O_{20}(OH)_4$	Gibbsite,* $Al(OH)_3$ Diaspore,* $HAlO_2$
Dickite, $Al_2(Si_2O_5)(OH)_4$	Montmorillonite, $(Al_{1.67}Mg_{0.33})Si_4O_{10}(OH)_2$ ($Na_{0.33}$)	Bravaisite, $Al_4K_X(Si_{8-X}Al_X)O_{20}(OH)_4$	
Nacrite, $Al_2(Si_2O_5)(OH)_4$	Beidellite, $Al_{2.17}(Al_{0.83}Si_{3.17})O_{10}(OH)_2$ ($Na_{0.33}$)	Brommallite, $Al_4Na_X(Si_{8-X}Al_X)O_{20}(OH)_4$	
Anauxite, $Al_{2-n}(Si_{2+n}O_5)(OH)_4$	Nontronite, $(Fe_{2.00})Al_{0.33}Si_{3.62})O_{10}(OH)_2$ ($Na_{0.33}$)	Attapulgite, $(Mg_5Si_8)O_{20}(OH)_2 2H_2O$	
Endellite, $Al_2(Si_2O_5)(OH)_4 2H_2O$	Saponite, $Mg_3(Al_{0.33}Si_{3.62})O_{10}(OH)_2$ ($Na_{0.33}$)	Ordovician bentonites	
Halloysite, $Al_2(Si_2O_5)(OH)_4$	Hectorite, $(Mg_{2.67}Li_{0.33})Si_4O_{10}(F, OH)_2$ ($Na_{0.33}$)	(Most of the minerals in this group are not very specific)	
Allophane, Amorphous	Sauconite, $Zn_3(Al_{0.33}Si_{3.67})O_{10}(OH)_2$ ($Na_{0.33}$)		

* These minerals are not usually considered among the clay minerals but when finely ground, behave like clays in ceramic processes.

versally accepted. In refractory clays, clay minerals are seldom found other than kaolinite, diaspore, and gibbsite.

The identification of the clay minerals, in many cases, is difficult because of their small size and indefinite composition. Petrographic methods can be used for the coarser grains. X rays may be used to identify the finer fractions with a considerable degree of certainty, especially if specimens are prepared with a preferred orientation of the crystals. Another useful method is thermal analysis, which can be made to give quantitative values, in some cases when the mineral is present in amounts as low as 1 per cent by weight of the total.

If the clay mineral is placed in a furnace beside a neutral body, such as alumina, and heated at a uniform rate (12°C per min), a temperature difference between the two that can be detected by a differential thermocouple will occur at different stages of the heating. The temperatures at which these differences occur are characteristic of the various clay minerals and serve as a means of identification even when they are mixed with others. A convenient apparatus is shown in Fig. 5 for this purpose. Figure 6 gives the differential temperatures for kaolinite, gibbsite, and diaspore plotted against the true temperature. The large endothermic peaks are caused by the energy required to expel the chemically combined water (the OH groups). The area under these peaks can be used as a quantitative measure of the amount of that particular clay mineral. The areas for a 0.4-g sample are as follows:

Mineral	Area, °C × Seconds
Kaolinite	11,700
Diaspore	11,150
Gibbsite	21,800

As an example, consider the thermal curve for a Dutch Guiana clay in Fig. 6. It will be noted that the peaks corresponding to kaolinite and diaspore, which are of small magnitude, occur at the temperatures of the initial parts of their respective reactions and not at the maxima. The area of kaolinite reaction is 700, for the diaspore 700, and for the gibbsite 19,200. This represents 6 per cent kaolinite, 6 per cent diaspore, and 88 per cent gibbsite. When these are converted to silica and alumina, 2.8 and 64.6 per cent are obtained, respectively, as compared with 4.5 and 58.4 per cent from a chemical analysis. If the 3.2 per cent Fe_2O_3 in the chemical analysis is counted as Al_2O_3, the agreement is good. Recent work has indicated that in some cases where the minerals are fine and intimately mixed, quantitative analysis by this method is difficult. Howie and Lakin[153] show that this method is also applicable to the analysis of limes, dolomites, and magnesites. Some recent work indicates that thermal analysis may also be used to identify the type of organic matter in a clay.

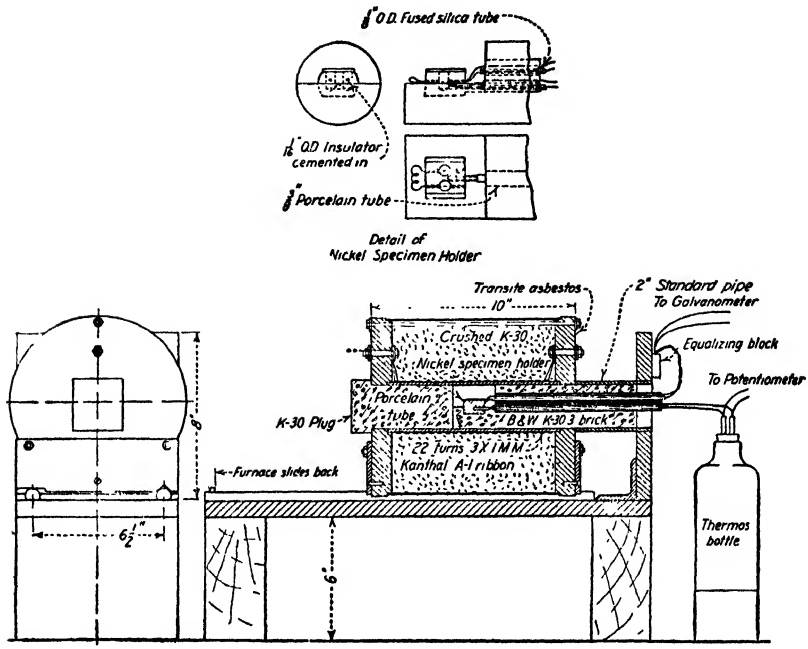


FIG. 5. Differential thermal apparatus. (*J. Am. Ceram. Soc.*)

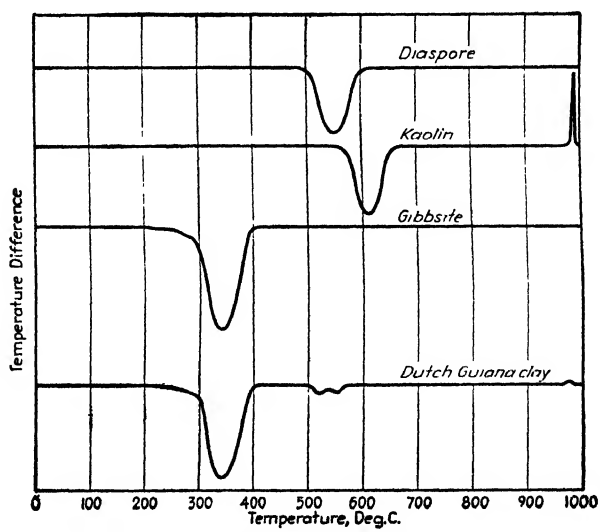


FIG. 6. Thermal curves of clay minerals.

The Exchangeable Bases. Attached to the broken corners and perhaps faces of all clays are ions that are not really part of the crystal structure but are held in place by unsatisfied bonds in the unbalanced lattice and thus can be replaced by other ions. The finer the particle size of the clay the more area is present for the attachment of these cations and the greater the so-called "base-exchange capacity," which is expressed in milliequivalents per 100 g of dry clay. The exchange ions can be replaced

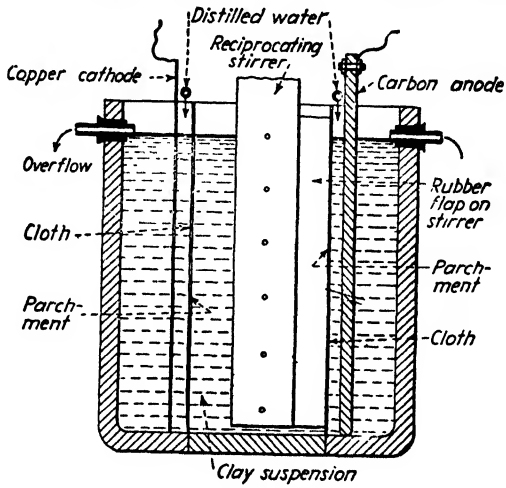


FIG. 7. Three-compartment dialysis cell.

by H^+ and OH^- on a clay by a number of methods, one being the treatment in a dialysis cell shown in Fig. 7. The clay slip, containing 5 per cent solids, is treated for about two weeks, the liquid in the end cells being replaced with distilled water at frequent intervals until a constant value of current is reached. Even with this long treatment there is reason to believe that many adsorbed ions or groups cannot be entirely removed. To produce a really clean clay calls for a more elaborate procedure. The liquid from the end cell can be evaporated and analyzed for the elements extracted. The exchangeable metallic bases reported by Graham and Sullivan[53] for several clays are shown below.

Clay	Exchangeable metallic bases				
	Ca	Mg	Na	K	Total
Georgia kaolin.....	0 4	0.6	0.1	Trace	1.1
Pennsylvania flint clay.	2.5	1 8	0.5	0.4	5.2
Kentucky flint clay....	3 4	2.0	0.9	0.8	7.1
Kentucky ball clay....	7 1	3.8	0.5	0.4	11.8

The total base-exchange capacity is believed in general to be as follows:

	Milliequivalents per 100 g
Kaolin	2–6
Ball clay	10–20
Bentonite	50–100

After a hydrogen clay is produced by dialysis, ions in any amount up to the saturation point can replace the hydrogen and hydroxyl group to give a clay with controlled adsorbed ions. The type of ion present in the clay profoundly influences its physical properties, producing a variable that has not generally been taken into account in the past. Just one example will bring this out for a fine-grained kaolin.

Milliequivalents of Na^+ per 100 g of Clay	Dry Strength Modulus of Rupture, lb psi
0 (hydrogen clay)	430
7	700
14	1,000

The control of exchangeable bases is particularly important when using clays in casting slips.

Organic Matter. Many clays contain appreciable amounts of organic matter, such as lignite or humic acid. Dark ball clays and less pure bog clays contain especially large amounts. Although little scientific work has been carried out to determine the influence of this matter on the properties of the clay, it is generally agreed that it does influence the plasticity, dry strength, and slip-forming properties, either because of an organic colloid or because of the organic acid. This is an important field for research; the ceramist, the organic chemist, and the soil chemist should cooperate more closely along these lines in the future. Nearly all organic matter can be removed by long digestion with 30 per cent hydrogen peroxide. The only paper treating this subject thoroughly is by Sharratt and Francis.[58]

The aging of clays, though little practiced in the refractories industry, is connected to some extent with bacterial action in the clay mass, which produces substances acting much like the organic acids.

Accessory Minerals. All clays contain mineral fragments of a nonclay type that have an important influence on the properties of the clay. The minerals commonly found are as follows:

Quartz
Feldspars (orthoclase, plagioclase)
Micas (muscovite and biotite)
Iron minerals (hematite, magnetite, limonite, pyrite, siderite)
Titanium minerals (rutile, anatase)
Limestone (calcite, dolomite)

Magnesite
Gypsum
Garnet
Tourmaline

A few of these minerals, such as quartz, act as a refractory nonplastic, whereas the others act more or less as fluxes and reduce the refractoriness of the clay.

Physical Properties. Only within the last few years has it been possible to measure the full range of particle sizes in clays with assurance. The size distributions for a few typical clays are shown in Fig. 8. It will be

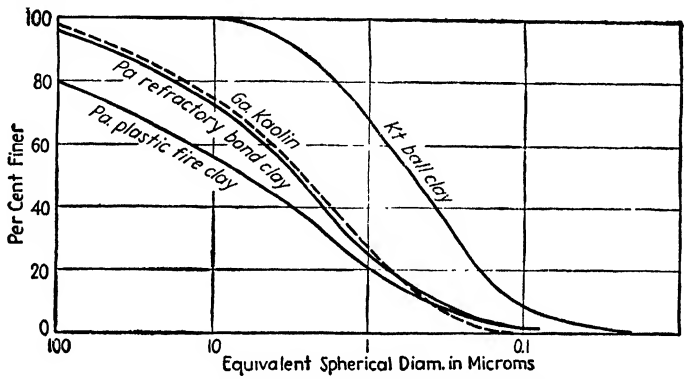


FIG. 8. Particle size distribution for various clays.

noticed, first, that there are few particles below 0.1 μ but a large portion are below 10 μ. As the surface area increases enormously with even a slight increase in the proportions of fines, careful measurements are needed in this range. It will be noted that the plastic fireclays, though coarser than the kaolin in the larger size range, have more very fine particles, which accounts for their relatively greater plasticity.

In order to study the influence of grain size on the physical properties, it is most convenient to split a clay up into a number of nearly monodisperse fractions for which the mean size can be accurately determined. It will be found that most of the physical properties vary with the particle size, as shown by Whittaker[57] in Table 7 for a clay containing wholly kaolinite.

The plasticity, or workability, varies greatly among clays. In general, the finer grained clays, free from nonplastics, are most plastic. The plasticity of most clays can be increased by fine grinding, aging, adding organic matter, or mixing in another clay of fine-grain size, such as bentonite.

Whereas some clays readily slake in water, others will remain under water indefinitely without breaking down. The flint clays and shales

TABLE 7. VARIATION OF PHYSICAL PROPERTIES WITH PARTICLE SIZE

Mean diameter, microns	Surface area per 100 g, sq cm	Drying shrinkage, per cent	Dry strength, psi	Relative plasticity
8.50	13×10^4	0.0	4.6	None
2.20	392	0.0	14.0	None
1.10	794	0.6	64.0	4,400
0.55	1,750	7.8	47.0	6,300
0.45	2,710	10.0	130.0	7,600
0.28	3,880	23.0	458.0	8,200
0.14	7,100	30.5	296.0	10,200

consolidated by chemical action cannot be broken down without considerable grinding, but a plastic fireclay will quickly disperse into its ultimate particles when added to water. Undoubtedly the adsorbed ions have an important influence on the slaking. For example, a hard and a soft kaolin of the same chemical composition, both containing wholly kaolinite, show, in the first case, ten times as much exchangeable calcium ions as in the latter.

In general, the fine-grained plastic clays have a high shrinkage, because they have large numbers per unit distance of interparticle water films, whose elimination causes the shrinkage. Montmorillonite, the mineral in bentonite, increases in the distance between the atomic planes of a single crystal by water molecules entering the crystal structure. This is the reason for the great swelling power of some bentonites.

The finer grained clays generally have high dry strengths, but other factors such as adsorbed ions and organic matter are important. As yet, we have little explanation of the forces holding the particles together in a dry clay. This is a field for interesting research.

The color of clay is of no great importance in refractories manufacture, except as an indication of impurities.

Kaolin $(OH)_4Al_2(Si_2O_5)$. Pure kaolin has a fusion point of 1785°C (3245°F), although this may drop a few degrees if any impurities are present. The residual or true kaolin occurs in many localities in rather small deposits in the Southeastern United States. There are also a few deposits in Vermont and Massachusetts, and Wilson[28] describes some producing deposits in the Pacific Northwest. The most workable deposits are the sedimentary or plastic kaolins, which are rather widely distributed in this country in the Southeastern states, where the beds are of great extent, averaging from about 15 to 30 ft in thickness with about the same thickness of overburden. The kaolin is usually mined by stripping off the overburden and taking out the clay by hand or with a power shovel. There

are considerable deposits of kaolin in England, which are mined as English china clay. Excellent deposits also occur in Czechoslovakia and Germany. Typical analyses of some kaolins are given in Table 8, and deposits are shown in the maps of Figs. 9 and 10.

TABLE 8. ANALYSES OF TYPICAL KAOLINS

Constituent	Georgia kaolin, per cent[192]	English china clay (washed), per cent	Vermont residual kaolin, per cent[22]	North Carolina kaolin (washed), per cent
Silica, SiO_2	45.8	48.3	58.0	45.8
Alumina, Al_2O_3	38.5	37.6	26.9	36.5
Titanium oxide, TiO_2	1.4		1.4	0.0
Ferric oxide, Fe_2O_3	0.7	0.5	1.5	1.4
Calcium oxide, CaO	Trace	0.1	0.4	0.5
Magnesium oxide, MgO	Trace		0.9	
Alkalies		1.6	2.2	0.3
Combined water	13.6	12.0	8.9	13.4
Total	100.0	100.1	100.2	97.9

Clays and Minerals Related to Kaolin. There are a number of other hydrated aluminum silicates of the kaolin group, most of which are rare.

Halloysite, $(OH)_4Al_2(Si_2O_5)$, occurs as a fine-grained, soapy, white clay. This mineral has often been confused with fine-grained kaolinite but can be distinguished by its thermal curve,[79] or by an electron microscope photograph, as the very fine particles are lathlike. A typical analysis is shown in Table 9.

TABLE 9. ANALYSES OF MINERALS RELATED TO KAOLINITE

Constituent	North Carolina halloysite, per cent	Allophane I, per cent[192]	Allophane II, per cent[192]
Silica, SiO_2	44.3	43.3	32.5
Alumina, Al_2O_3	37.4	39.9	46.5
Ferric oxide, Fe_2O_3	0.4		0.7
Lime, CaO	0.2	0.7	0.4
Magnesia, MgO	0.1		0.5
Alkalies	0.2	0.6	
Water of constitution	15.1	15.5	19.4
Total	97.7	100.0	100.0

Allophane, or indianaite, is a waxy white clay found in Indiana and Kentucky with the composition shown in Table 9. It is so fine grained as to be amorphous.

Several other members of the kaolinite group of rare occurrence are mentioned in the tables at the end of the chapter.

Ball Clays. Ball clays are distinguished by their fine grain, lignite content, and high plasticity but are not usually so refractory as kaolins, the

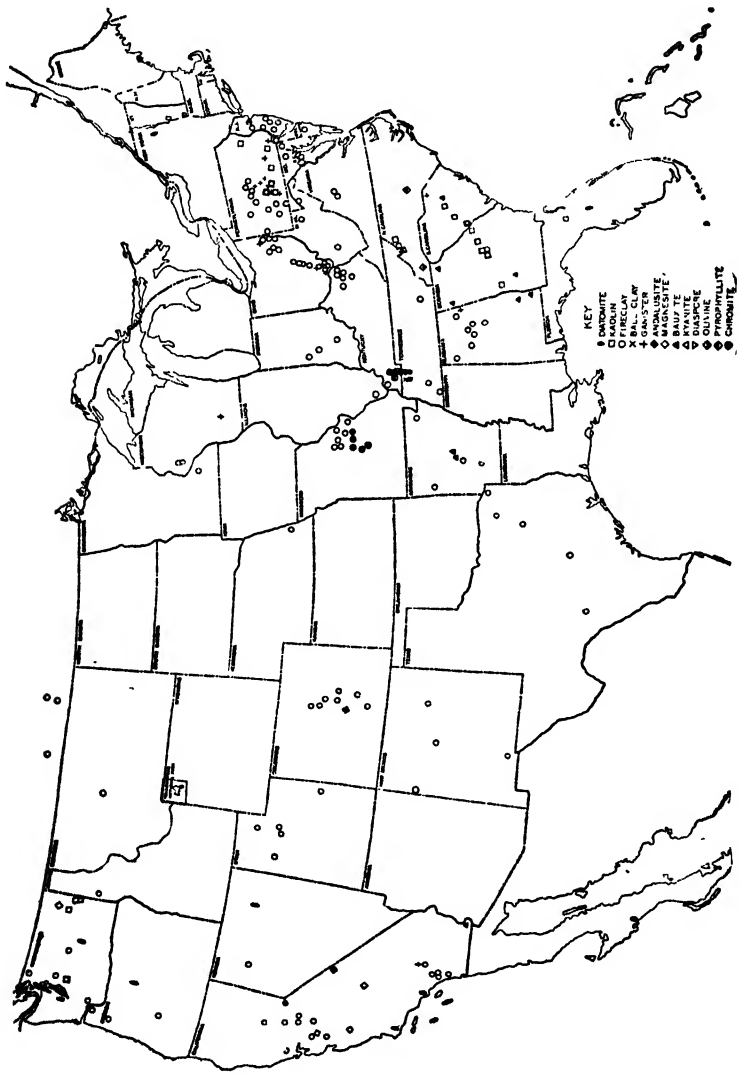


FIG. 9. Working deposits of refractory materials in the United States. (*Copyright, American Map Company, Inc., New York. No.* 10,074.)

fusion point being around 1675°C (about 3050°F). They are sometimes used in refractories as a bond for harder and less plastic clays, but their greatest use is in whiteware. The analyses of two typical ball clays are given in Table 10. They are found almost exclusively in Kentucky and Tennessee as shown in Fig. 9.

Fireclays. The so-called "fireclays" include nearly all clays that have a fusion point above approximately 1600°C (about 2900°F) and are not

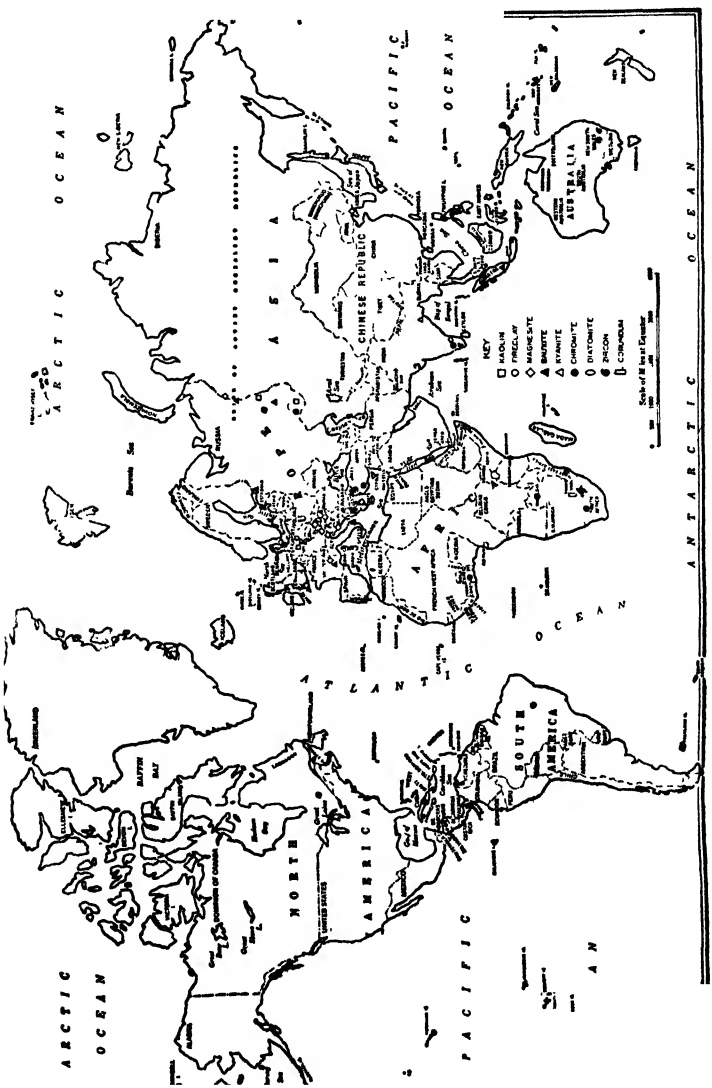


FIG. 10. Important deposits of refractory materials in the world. (*Copyright, American Map Company, Inc., New York, No.* 10,074.)

white burning. Fireclays are widely distributed and vary greatly in their characteristics. They may be roughly divided into the following types: flint clays, which (owing to great pressure encountered since they were deposited) are compressed into a hard, rocklike mass and require fine grind-

TABLE 10. ANALYSES OF BALL CLAYS

Constituent	Mayfield, Ky., per cent[192]	Tennessee, per cent
Silica, SiO_2	56.4	46.9
Alumina, Al_2O_3	30.0	33.2
Ferric oxide, Fe_2O_3		2.1
Lime, CaO	0.4	0.8
Magnesia, MgO	Trace	
Potash, K_2O	3.3	0.7
Soda, Na_2O	2.0	
Titanium oxide, TiO_2		
Water (combined)	7.9	16.5
Total	100.0	100.2

TABLE 11. ANALYSES OF FIRECLAYS
(Analyses by Downs Shaaf)

	Plastic, Lawrence, Ohio	Flint, Cambria, Pa.	Flint, Carter, Ky.	Semi-flint, Jackson, Ohio	Semi-flint, Clearfield, Pa.	Plastic, Vinton, Ohio	Flint, Montgomery, Mo.
SiO_2	58.10	44.43	44.78	50.32	43.04	46.72	44.04
Al_2O_3	23.11	37.10	35.11	31.53	36.49	33.06	38.03
Fe_2O_3	1.73	0.46	1.18	1.02	1.37	0.68	0.63
FeO	0.68	0.55	0.74	0.35	0.83	0.55	0.22
FeS_2	0.55	0.22	0.14	0.12	0.24	0.34	0.01
MgO	1.01	0.19	0.55	0.18	0.54	0.19	0.12
CaO	0.79	0.60	0.77	0.80	0.74	0.61	0.40
Na_2O	0.34	0.10	0.29	0.07	0.46	0.42	0.10
K_2O	1.90	0.55	0.44	0.05	1.10	1.53	0.22
H_2O-	2.27	0.80	0.84	2.47	0.82	2.21	0.78
H_2O+	7.95	12.95	13.07	11.25	12.44	11.50	13.55
CO_2	0.05	0.11	0.07	0.14	0.05	0.02	0.04
TiO_2	1.40	1.84	2.22	1.45	1.79	2.20	1.82
P_2O_5	0.17	0.21	0.02	0.48	0.10	0.12	0.28
SO_3	0.03	0.01	0.01	0.01	0.01	0.01	0.01
MnO	0.01	0.01	0.02	0.02	0.01	0.01	0.01
ZrO_2	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Org. C	0.22	0.10	0.11	0.07	0.22	0.04	0.01
Org. H	0.03				0.03		

ing to develop plasticity; plastic clays, which are soft and easily tempered into a plastic mass; and refractory shales, which can usually be made directly into brick without the addition of bonding clay.

Analyses of a number of types of fireclays are given in Table 11, and the distribution in the United States on the map of Fig. 9.

Super-duty fireclay brick are usually made from pure Missouri flint clays with approximately the composition in Table 11. They have a low porosity and show little or no reheat shrinkage.

2. Clays and Minerals High in Alumina. *Hydrated Alumina.* Some of the most important refractory materials are those containing the mineral diaspore, ($HAlO_2$) usually occurring with kaolinite in varying proportions. The clays vary from nearly pure diaspore to mixtures containing nearly all kaolinite. Most of them occur in Missouri, although there are a few other minor locations. From these clays are made the high-alumina brick having alumina contents of 50, 60, 70, and 80 per cent according to the classification. They may also have some corundum added.

FIG. 11. A gibbsite nodule cut in half; about one-fourth natural size.

There are other high-alumina clays containing gibbsite [$Al(OH)_3$] or mixtures of gibbsite and kaolinite. The purer materials, such as those from Dutch Guiana (Fig. 11), contain almost all gibbsite, but the aluminous clays from the South have more or less kaolinite mixed with them. The term "bauxite" is used here for clays containing a mixture mainly of kaolinite and gibbsite. The bauxitic clays have not been used for refractories to any extent because of their less favorable shrinkage properties, but may come into use as the diaspore becomes exhausted.

The locations of the principal deposits of high-alumina clays are shown in Figs. 9 and 10. Both the chemical and mineral analyses of some typical high-alumina clays are shown in Table 12. The thermal method is particularly valuable in studying these clays because it readily distinguishes between diaspore and gibbsite.

Sillimanite Types of Minerals. There are a number of minerals having a composition Al_2SiO_5, which gives a silica content of 37 per cent and an alumina content of 63 per cent. Sillimanite occurs in a number of small deposits in this country, such as California, North and South Carolina, and Georgia, but the largest source of supply is in India. Andalusite has

a different crystal form from sillimanite and is found in small deposits in California and in considerable quantities in Spain. Kyanite occurs in India, in some of the Southern states, and on the West Coast of the United States. All these minerals are decomposed to mullite and silica on heating above 1555°C (about 2830°F) when pure and at a lower temperature when fluxes are present. These materials are being used to a considerable extent as refractories at the present time but commercially are

TABLE 12. HIGH-ALUMINA CLAYS

Clay	Dutch Guiana gibbsite	First-grade diaspore, Mo.	Bauxite, Ga.	Burley, Flint, Mo.	Second-grade diaspore, Mo.
Chemical Analyses					
Silica	4.5	10.9	26.0	33.8	29.2
Alumina	58.4	72 4	54.0	49 4	53 3
Titanium oxide	2.9	3.2	2.1	2 6	2.7
Iron oxide	3.2	1.1	1.0	1.8	1.9
Lime	0.4				
Magnesia					
Alkalies					
Combined water	30.6	13.5	16.1	12.0	12 0
Total	100 0	101.1	99.2	99.6	99 1
Thermal Analyses					
Kaolinite	6	None	67	71	18
Diaspore	6	90	None	26	53
Gibbsite	88	None	38	None	None

often confused one with another. The great problem is to concentrate[119] the ore efficiently and at the same time provide fairly coarse grains. Thin sections of these minerals are shown in Figs. 12, 13 and 14.

Topaz. This mineral has been found in India in some quantity, and recently an important deposit has been discovered in South Carolina.[121] Topaz has the composition $Al_2SiO_4(F,OH)_2$ and thus will readily transform to mullite on firing, hence offering attractive possibilities as a raw material.

Pyrophyllite. This talclike mineral is found in a number of deposits in the South and has been used in some refractories in place of clay. Its formula of $(OH)_2Al_2(Si_2O_5)_2$ does not give so high an alumina content as kaolin. However, it has been successful in some cements and plastics.

Forms of Alumina. Alumina occurs in a number of forms. The α-alumina is identical with the natural mineral corundum (Fig. 15), which

is a trigonal crystal with a specific gravity of 4.0. This mineral apparently is very stable and is almost always produced from cooling fusions. γ-alumina is hexagonal but has a spinellike structure and a specific gravity of 3.31 and is generally formed by the heating of hydrous alumina materials such as kaolin or gibbsite. At higher temperatures, it slowly inverts to the α-form. An isometric form of alumina has been described having a specific gravity of 3.47 and is found in some quickly cooled melts. Apparently this form is not found to any extent in refractories.

FIG. 12. Thin section of sillimanite. (250×)

The so-called "β-alumina" has been found by Beevers and Ross[118] to be not a form of alumina but a compound consisting of 11 molecules of Al_2O_3 and 1 molecule of soda or potash. A "ζ-alumina" has been described as occurring only in melts containing lithium. Probably this is similar to the β-alumina, being a compound of lithium oxide and alumina.

Corundum. Corundum, or emery, Al_2O_3, is found in many small deposits, the most important being in Asia Minor, South Africa, Greece, Ontario, and North Carolina. It has not been used to any extent for a

refractory but would seem to be a material worth more investigation. Crystalline alumina made in electric furnaces is used to a considerable extent as a refractory.

3. Silica Minerals. *Ganister.* The most commonly used silica mineral for refractories is ganister, a common name for true quartzite. Not all quartzites are suitable for making refractories, as they must be of high purity and have good mechanical strength. The principal deposits of

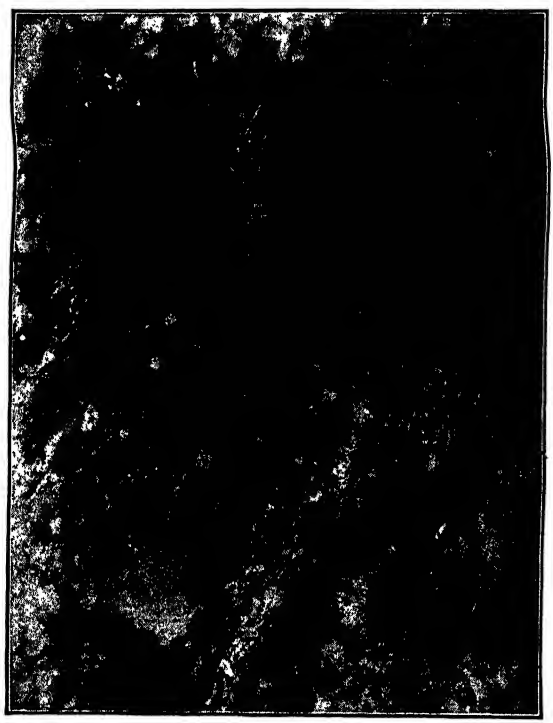


FIG. 13. Thin section of andalusite; 250×, with crossed Nicol prisms and gypsum plate.

ganister in this country are the Medina sandstone of Pennsylvania, the Baraboo quartzite of the Devil's Lake region, Wisconsin, and the quartzites of Alabama and Colorado. A quartzite is usually mined from the bodies of talus, or slide rock, occurring on the mountain slopes. A few typical analyses of quartzites are given in the following table, and a thin section is shown in Fig. 16.

The fusion point of quartzite[127] is very close to 1700°C (about 3090°F); and like mullite, it shows little softening below its melting point. This is its chief value when used as a refractory, as it retains its resistance to load at higher temperatures than fireclay materials. Owing, however,

to their high thermal expansion, silica materials are very sensitive to temperature changes in the low-temperature ranges. Most silica refractories are made in the form of bricks or special shapes, but some ganister

TABLE 13. ANALYSES OF QUARTZITES

Constituent	Medina quartzite, per cent[124]	Baraboo quartzite, per cent[124]	Alabama quartzite, per cent[124]	Sharon conglomerate[132]
Silica, SiO_2	97.8	98.2	97.7	98.0
Alumina, Al_2O_3	0.9	1.1	1.0	0.9
Ferric oxide, Fe_2O_3	0 9	0.2	0.8	0.9
Lime, CaO	0.1	0.0	0 1	0.3
Magnesia, MgO	0.2	Trace	0.3	Trace
Alkalies, K_2O, Na_2O	0.4	0.1	0.3	0.2
Total	100.3	99.6	100.2	100.3

FIG. 14. Thin section of kyanite. The large crystal on the left border is kyanite which shows pronounced cleavage and numerous inclusions. The rest of the field shows a grain of stauralite, three smaller garnet crystals with muscovite, biotite, quartz, feldspar, and magnetite; 40×, with ordinary transmitted light.

is used in rammed furnace bottoms. Recently quartzites have been washed to bring the total impurities below 0.5 per cent for super-duty silica brick.

Firestone. Natural stone refractories are still used to some extent. They consist of an easily cut sandstone[134,135,136] or a mica schist. In either case, the stone must have a certain flexibility of structure to reduce the tendency to spall. Firestone is rather wide in occurrence, working

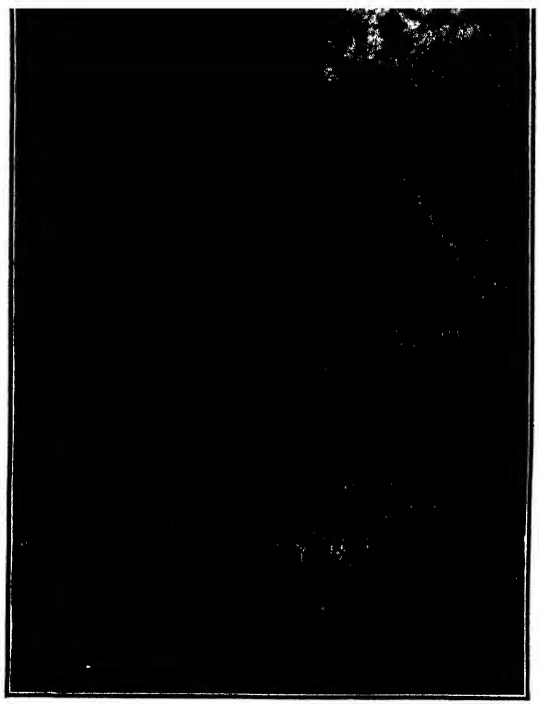


FIG. 15. Thin section showing appearance of corundum crystals formed in the electric furnace; 80 ×, with crossed Nicol prisms.

deposits being found in Pennsylvania, Tennessee, Ohio, and several other states.

Sand. A small amount of beach sand is used for furnace bottoms, as, for example, in the hearth of malleable-iron melting furnaces, but the volume used is very small compared with the refractories made from quartzite. In Europe, glass sand is ground and added to quartzite in the making of silica brick, mainly to increase the purity.

Diatomaceous Earth. Another type of siliceous mineral, used mainly as a heat insulator, is diatomaceous earth (infusorial earth or kieselguhr),

a widely distributed material. It is composed of the skeletons of diatoms, which are microscopic organisms (Fig. 17). The desirable characteristics of this material are its closed cells and high porosity, which gives a low

FIG. 16. Thin section of quartzite. The light and dark areas in this photomicrograph show quartz grains at different orientation with respect to the plane of polarization of the Nicol prisms; 80×, with crossed Nicol prisms.

TABLE 14. ANALYSES OF DIATOMACEOUS EARTHS

Constituent	Oberhole, Germany, per cent	California, per cent
Silica (SiO_2)	87.9	85.3
Alumina (Al_2O_3)	0.1	5.4
Ferric oxide (Fe_2O_3)	0.7	1.1
Calcium carbonate ($CaCO_3$)	0.7	1.1
Organic matter	2.3	
Water	8.4	5.6
Total	100.1	98.5

density and a low thermal conductivity. Analyses of two typical samples of infusorial earth are given in Table 14.

4. Magnesite and Lime. Magnesite refractories are of great importance in the metallurgy of steel and nonferrous metals, as they are used almost exclusively for the part of the furnace that comes in contact with the molten metal and slag, a large volume being used in the bottoms of the basic open-hearth furnaces in the form of lumps and brick.

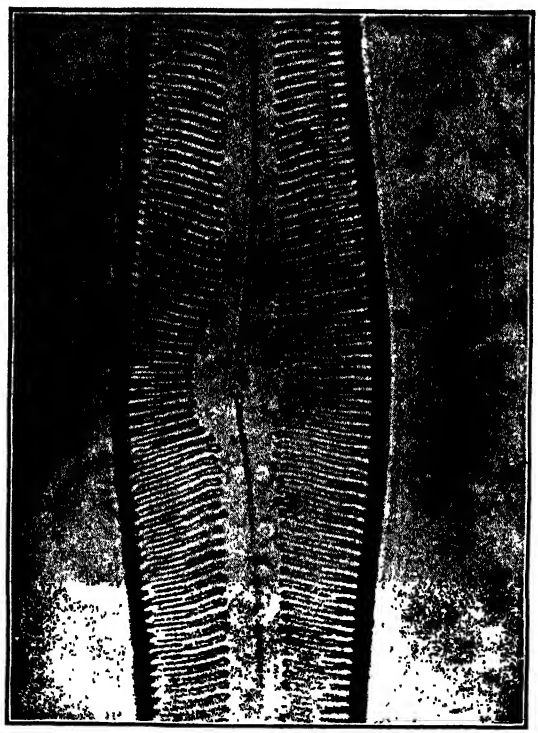


FIG. 17. Photomicrograph of a single diatom showing fine cell structure. This structure is the reason for the excellent heat insulating properties which diatomaceous earth possesses; 800×, with ordinary transmitted light.

Magnesite. Magnesite occurs in nature as the carbonate, and two types have generally been recognized, the crystalline and the dense, the latter usually being of greater purity. The crystalline material is found in considerable quantity in Austria, Russia, Manchukuo, Quebec, and the state of Washington. Figures 10 and 9 show the important deposits. The Austrian material usually runs rather high in iron and has been in great demand for metallurgical work because it will frit together into a solid mass at available temperatures. The magnesite from Quebec runs

higher in lime. The Washington magnesite occurs in large quantities and is relatively pure.

The dense type of magnesite usually occurs in veins and lenses, the most important deposits being found on the island of Euboea off the coast of Greece. The purity of this deposit, if carefully selected, is high, running between 94 and 98 per cent magnesium carbonate. Several California deposits have been operating for a number of years and give a pure material. Magnesite from sea water in California and Texas [148,149,150] is now assuming importance. Magnesia can also be produced from dolomite such as by the Pike process.[154]

TABLE 15

Constituent	Austrian	Austrian	Manchukuo	Washington	Greece	California sea water
SiO_2	5.8	1.0	3.7	4.9	6.6	5.1
Al_2O_3	1.7	1.0	1.0	1.5	4.4	0 5
Fe_2O_3	4.0	6.9	1.5	3.4		0.2
CaO	5.0	2.1	1 6	2 8	2.4	1.8
MgO	83.0	88.6	92.0	87.1	86.4	91.7
Ignition loss	0.2	0.3	0.1	0.1	0 2	0.3
Total	99.7	99.9	99.9	99.8	100.0	99.6

Several analyses of burned magnesite are given in Table 15, and a thin section is shown in Fig. 18.

Magnesite is produced as caustic-burned and dead-burned material. The latter is used for refractories and is fired at 1550 to 1750°C (about 2820 to 3180°F) to drive off practically all the CO_2 and form crystals of periclase. An excellent description of the production of dead-burned magnesite is contained in P.B. 37804.[151] The high-iron magnesites are sufficiently magnetic to make concentration by magnetic separators an efficient process. Some of the purer magnesites have iron added by the Alterra[151] process, where calcium ferrite is made and combined with the magnesite in a rotary kiln at 1500°C (about 2732°F). Magnesite can be fused in the electric furnace and, on cooling slowly, forms relatively large periclase crystals.

Dolomite. Dolomite is a solid solution of calcium and magnesium carbonate and, when pure, has an equal number of molecules of both, although all ratios occur in nature. Dolomites are very widely distributed. They have been used to some extent to replace magnesite in open-hearth bottoms but, because of their slaking properties, are not so good as magnesite. Although many experiments have been made on the production of

a successful dolomite brick, as yet all the difficulties have not been overcome.

Lime. Lime, next to magnesite, is believed to be the most refractory commercial oxide and is very widely distributed in deposits of great purity. However, little success has been had with this material as a refractory, for it slakes readily in both air and water. However, if lime is heated to 1800°C (about 3270°F) in an oxidizing atmosphere, it can be crystallized and in this form has a considerable resistance to slaking.

FIG. 18. Thin section of crystalline magnesite. This section shows the high relief and cleavage which this mineral possesses; 80×, with crossed Nicol prisms.

Olivine, Mg_2SiO_3. This magnesium silicate usually has 5 to 8 per cent of the MgO replaced by FeO in the theoretical formula. By mixing with the correct amount of magnesite, this material has been used in the last few years to make forsterite refractories. Olivine deposits are widespread, but excellent material occurs in the dunite rock of North Carolina.

5. Chromite. The commercial chrome ore contains a solid solution of spinels closely approximating

$$\begin{matrix} Cr_2O_3 & \diagdown\diagup & FeO \\ Al_2O_3 & \diagup\diagdown & MgO \end{matrix}$$

In most cases, the spinel is balanced, but some cases have been reported where either the R_2O_3 or the RO is somewhat in excess; however, this may be due to difficulty in obtaining uncontaminated chromite grains for analysis. The chromite is always associated with a gangue chiefly of serpentine but also containing small amounts of feldspars, silica, carbonates, etc. Chrome ores are believed to originate both from magmatic

FIG. 19. This photomicrograph is a thin section of chromite with some serpentine associated with it. The chromite is the darker-colored areas, which show very irregular cleavage. Chromite is nearly opaque, and the thin section must be very thin to render it transparent; 250 diameters and wave plate to give second order green, and photographed through a "B" Wratten filter (deep red).

crystallization and by formation from hydrothermal solutions. Concentration methods have not been used much in separating the gangue from the ore, but the addition of MgO will cause the formation of forsterite on firing and thus remove the low-softening siliceous compounds.[160] A thin section of a typical chrome ore is shown in Fig. 19. The outstanding papers by A. T. Green[165,166] and his associates on chrome ores in *Special Report* 32 of the Iron and Steel Institute should be consulted for more detailed information on this subject.

The largest supplies of chrome ore come from Rhodesia and New Caledonia. There are, however, considerable deposits in Turkey, Cuba, the Philippines, Russia, and Greece and small deposits in Canada, California, Oregon, and Alaska. The analyses of several chrome ores are given in Table 16.

TABLE 16

Constituent	Turkey	Rhodesia	Philippines	New Caledonia	Russia	Cuba
Cr_2O_3	46.6	45.4	32.1	54.5	46.2	30.5
SiO_2	6.7	7.5	5.3	3.1	4.0	6.1
Al_2O_3	12.5	13.8	27.6	11.0	14.6	27.5
FeO	12.9	15.1	13.0	19.5	15.6	14.2
CaO	1.2	0.5	1.1	1.5	0.3	0.9
MgO	17.3	13.6	18.2	8.0	15.4	18.3
Total	97.2	95.9	97.3	97.6	96.1	97.5

6. Less Common Refractory Oxides. Many of the so-called "rare elements" may occur in larger percentages than some of our useful metals but, as they are not concentrated at any one place, cannot be so readily extracted. The relative abundance of the refractory elements is shown in the chart of Fig. 20 plotted from the article of Pannell[179] with some additions. It will be seen that thorium and cerium, for example, are as plentiful as copper, and beryllium is as plentiful as cobalt.

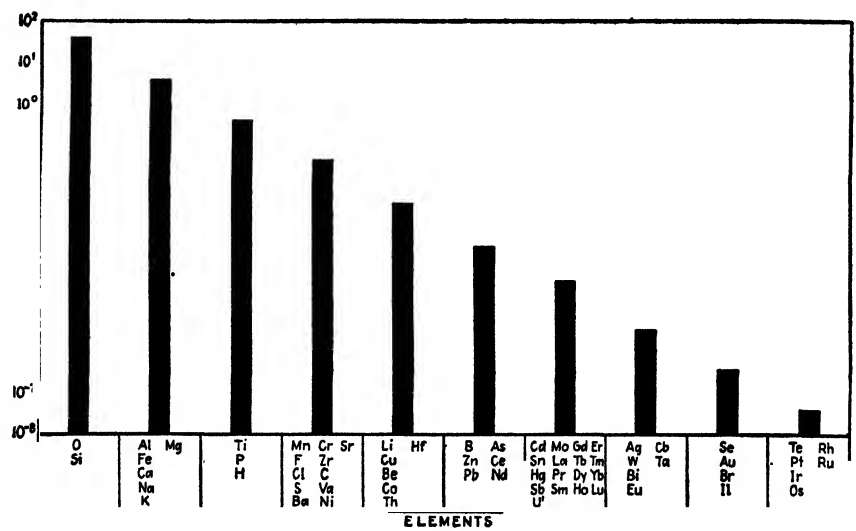


FIG. 20. Relative abundance of the refractory-forming elements in the earth's crust.

Zirconia. The most common minerals are zircite and baddeleyite with the formula ZrO_2. They are found in considerable deposits in Brazil and Ceylon with a ZrO_2 content of 50 to 80 per cent. An analysis of Brazilian baddeleyite is shown in Table 17.

Zircon, $ZrSiO_4$, is widely distributed, large deposits being found in India, Madagascar, and New South Wales. It is also plentiful in some beach sands of Florida and Australia from which it can be concentrated by tabling. An analysis of a typical sample is shown in Table 17. Both zirconia and zircon have been used for special refractories, their properties being discussed in Chap. XII.

TABLE 17. ANALYSES OF ZIRCONIUM MINERALS

Constituent	Baddeleyite, per cent	Zircon, per cent
Ferric oxide, Fe_2O_3	1.6	0.1
Alumina, Al_2O_3	7.8	1.4
Lime, CaO	0.0	
Silica, SiO_2	27.3	40.4
Zirconium oxide, ZrO_2	60.4	51.6
Undetermined	2.9	6 5
Total	100 0	100.0

Titania is widely distributed as rutile (TiO_2) or ilmenite ($FeTiO_3$). Titanium is really one of our abundant elements but is so dispersed that it seems rare.

Thoria. This is our most refractory oxide, occurring in the monazite sands and in some other deposits as shown in the map in Fig. 369, Chap. XXIV. The important producers are India, Brazil, Australia, and Ceylon. It has been used for crucibles in the melting of platinum metals. It is slightly radioactive and is a fissionable material, which will undoubtedly be restricted in the future.

Beryllia. This highly refractory oxide is produced mainly from the mineral beryl found in many pegmatites. The chief source of supply is Argentina, Brazil, and India.[178] The extraction of the oxide from the ore is discussed by Motock[181] and in references of Chap. XII.

Uranium Oxide. This is a fissionable material and will probably not be available as a refractory, but it is of interest in nuclear power development as discussed in Chap. XXIV. The published sources[180] of the ore are shown on the map in Fig. 369, Chap. XXIV.

The Rare Earths. These oxides are not so scarce as the name implies, as indicated in the chart in Fig. 20, but their separation, one from another, presents great difficulties. The only commercial ore for these materials

is monazite sand,[177] containing 6 to 9 per cent of ceria and lesser percentages of the other rare earths. Many of the rare earth oxides are quite refractory and may be of use in special cases.

7. Carbon. *Graphite.* Carbon in the form of graphite occurs naturally in many localities. In this country, the deposits are usually too small to make it practical to work them commercially. Large deposits occur in Ceylon, Madagascar, Korea, and Czechoslovakia. Artificial graphite is also manufactured to some extent by heating coke to a high temperature in an electric furnace. Graphite is mainly used in crucibles for melting metals.

Coal. Coal of both the anthracite and the bituminous varieties is widely distributed. Before use as a refractory or insulator in electric furnaces, it is coked to drive off the volatile matter. Petroleum coke is used for high-purity purposes.

8. Production and Price of Minerals in the Refractories Industry. In Table 18 are given the production figures and prices of many materials used for refractories as taken from the "Minerals Yearbook." Most of these figures are rounded off, and it should be realized that in some cases, restrictions prevent publication of complete values. In other cases, it is impossible to separate the figures into refractory and nonrefractory uses. Nevertheless some interesting deductions may be drawn from these data.

One of the most striking facts is the very small increase in price of many of the products between the years 1920 and 1945. For example, bauxite, dolomite, magnesite, fireclay, kaolin, and talc show very little variation in price over this period. This is accounted for by more efficient mining methods, offsetting the higher labor costs. On the other hand, products of more limited occurrence show some price increases, such as chromite, beryl, and tantalum concentrates.

Bauxite, a large part of which goes into the manufacture of aluminum, has shown increased production and importation in the last few years, and the same may be said of fireclay. On the other hand, the consumption of kaolin, partly used in the paper trade, has held rather constant, with domestic production increasing to take the place of the greatly decreased importation.

Magnesite is now largely from domestic sources, only small amounts being imported after 1922. On the other hand, except for the years 1942 and 1943, when shipping space was very scarce, most of the chromite was imported. Most of the tantalum ore, zirconium concentrates, and monazite sand is also imported.

The next generation may find many of our natural resources exhausted, and restrictions of others for military purposes may be expected.

9. Summary. In Table 19 there are assembled all the refractory minerals known. The fusion points and occurrence are shown wherever

TABLE 18. PRODUCTION STATISTICS FOR REFRACTORY MATERIALS

Year	Columbium and tantalum ore				Molybdenum metal contained in ore and concentrates				Platinum metals				Thorium ore and monazite sand				Uranium compounds				Zirconium concentrates			
	U.S. production, M pounds	Value of U.S. production, dollars/lb	Importations, M pounds	World production, M pounds	U.S. production, M pounds	Value of U.S. production, dollars/lb	Importations, M pounds	World production, M pounds	U.S. production, M pounds	Value of U.S. production, dollars/lb	Importations, M pounds	World production, M pounds	U.S. production, M pounds	Value of U.S. production, dollars/lb	Importations, M pounds	World production, M pounds	U.S. production, M pounds	Value of U.S. production, dollars/lb	Importations, M pounds	World production, M pounds	U.S. production, M pounds	Value of U.S. production, dollars/lb	Importations, M pounds	World production, M pounds
1920	4	0.36			35	0 49	16		3.5		8.4	15												
1921	3	0.38			355	1 08	30		4 7		6.5													
1922	0.6	0.40					412		4 9		9.2	15				46								
1923	1	0.54			23		17		4 2		8.9													
1924	1	0.60			297		10		5.5		9.2	17							13					
1925					1,154	0.83	2		4.2		10.5								19					
1926	2	0.32			8,498	0 72	13		7.1		11.3	17							53					
1927	1	0.38			2,286	0 81	13		3.8		12.4					1,194			68		8,000		4	
1928					3,329	0 58					11.3	17				885			165		0		864	
1929			15		3,905	0.58			4.0		12.9					1,154			273		0		2,689	
1930			8	12	3,759	0.55			3.7		11.6	25							231		0		3,039	
1931			6		3,157	0.50			3.0		10.9					3,396			180		0		1,124	
1932			36		2,373	0.50			1.5		4.7	17.4					3		122		0		27	
1933			14		5,761	0.75			4.3	294.00	13.5	18.2					2		186		0		569	
1934	2	0.48		400	9,377	0.69		4,400		264.00	14.5	34.4					7		159		0		1,706	
1935	8	0.57			10,892	0.67		6,600	3.5		13.7	32.3					22		296		0		5,757	
1936			498		17,959	0.67	0.1	1,100	3.9	384.00	17.5	35.8				4	18		341		0		11,565	
1937	16	0.81		1,500	30,122	0.68	8	15,400	3.8	372.00	17.2	39.6					21				0		1,800	
1938	36	0.97	687	1,500	25,727	0.70		35,200	3.0	408.00	13.4	45.1				902	52				0		4,000	
1939	0.3	0.88	166		32,415	0.68		33,000	3.4	432.00	25.6	45.0				2,000					0		6,000	
1940			1,085		25,329	0.68		37,400	3.9		16.3	38.8				6,000			2,640		400		34,000	
1941	0.3	0.88	1,843		38,377	0.78	4	44,000	12.7		25.8	40.3				6,000			388		400		56 000	
1942	0.2	0.88	2,329		66,437	0.71	750	61,500	33.4	625.00	28.0	65.5				8,000			918		400		68.000	
1943	15	1.87	3,025		53,955	0.71	1,789	68,200	27.9		30.2	51.6				10,000			211		400		56,000	
1944	10	2.40	4,520		39,423	0.71	3,499	44,000	12.7		29.7	41.7				768			10		400		48,000	
1945	6	2.30	5,000		32,524	0.71	665	35,200		370.00	31.9	50				1,100					4,000	$0.03	52,000	

TABLE 18. PRODUCTION STATISTICS FOR REFRACTORY MATERIALS (*Continued*)

Year	Kaolin (processed)				Kyanite, etc.				Magnesite (crude)				Pyrophyllite talc and ground soapstone				Titanium concentrates (ilmenite and rutile)				Tungsten ore and concentrates (60 per cent WO_3)			
	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons
1920	268	10.70	362						304	9.10	34		211	14.35	23		0.5				0.2	7.86	1.95	23
1921	163	9.70	163						48	10.65	52		122	14.40	12								1.62	9
1922	276	8.50	310						56	10.20	73	537	199	14.35	18		5						1.65	12
1923	337	8.70	311						147	7.50	5	512	197	15.30	20	234	7				0.2	10.00		13
1924	227	8.95	353						120	8.70	0.01	481	204	17.20	18	376	5	15.20			0.6	8.47		13
1925	367	8.80	373						121	11.80	0.49	717	182	11.10	21	363	6	16.60			1	10.57	0.43	20
1926	432	8.75	396						134	8.95	0.61	716	182	11.60	24	343	5	17.00		20	1	11.10	1.27	24
1927	454	8.40	339						121	9.00	0.86	833	192	11.60	25	428	4	10.50		12	1	10.37	1.08	8
1928	496	8.25	307						127	8.65	0.76	823	203	12.50	27	392					1	10.40		
1929	518	8.30	280						188	8.00	0.30	1,045	220	12.00	31	424				av	0.8	13.13		
1930	510	7.60	236						129	8.00	0.84	704	179	11.80	26	230			25	132	0.7	12.09		
1931	443	6.65	151						74	6.75	0.50	693	164	11.30					31		1	11.02		
1932	345	5.83	100						38	7.45	0.01	695	123	11.10	20	315			34	65	0.4	9.20		7
1933	411	5.75	116						108	7.75	0.01	880	166	10.45	22	425			39	79	0.9	9.58		12
1934	426	6.33	101									1,135	139	10.45	20	419			72	97	2	14.57	0.48	16
1935	524	7.20	126		4-8		1		177	6.73	0.05	909	173	10.70	24	275			116	272	2	13.37	0.45	22
1936	639	7.10	140						207	6.82	0.06	1,102	216	10.85	25	233			128		3	14.83	2	
1937	732	7.45	147				8		203	7.30	0.04		230	11.14	27	514			154	280	4			
1938	595	8.00	84				4		97	7.47	0 04		213	10.82	22	421			209	300	3			40
1939	781	7.95			3	23.00	4		199	7.35	0.54		254	10.63	26	447			256	85	4			38
1940	833	8.40	106		4	22.00	8		333	7.47	0.02		282	10.69	28	397	24	24.00	2	300	5			
1941	1,088	8.45	67		8	21.00	14		374	7.10			416	11.29	15	459	26	26.60	6	240	7	14.00	13	
1942	1,088	8.45			9	21.80	7		497	7.80			387	12.25		434	80	27.75	11	220	9	14.50	15	
1943	929	8.70	55		10	24.80	10		754	8.05			412	12.40		432	208	21.40	14	300	12	16.30	19	
1944	873	9.00	46				6		561	7.85	1		398	12.58	8	377	286	29.60	10	310	10	14.00	19	
1945	940	9.68	57						336	6.93			401	12.36	6		316	26.20	10	300	6	14.00	9	

TABLE 18. PRODUCTION STATISTICS FOR REFRACTORY MATERIALS (*Continued*)

Year	Bauxite (crude ore)				Beryllium ore (beryl)				Chromite				Dolomite (dead burned)				Fireclay				Graphite (natural)			
	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons	U.S. production, M short tons	Value of U.S. production, dollars/short ton	Importations, M short tons	World production, M short tons
1920	583	5.58	43	1,000					3.3	13.65	1,922		1,580				2,262	3.12			9	69.50	21	
1921	157	5.67	28	350					0.3	9.45	655		499				1,196	2.98			2	48.50	8	
1922	347	5.79	24	900					0.4	18.50	741		1,074				1,679	2.76			3		12	
1923	587	5.38	119	1,200					0.3	15.30	130	202	1,226				2,298	2.86			6	35.80	19	98
1924	390	5.48	202	1,155					0.3	35.60	118	288	1,239				2,444	2.75			5	17.60	16	97
1925	355	5.58	354	1,386					0.1	17.50	150	307	1,425				2,567	2.85			5	19.40	18	121
1926	440	5.49	282	1,257					0.2	21.30	215	362	1,480				2,819	2.88			5	45.00	16	132
1927	247	8.06	357	1,416					0.2	23.00	222	410	1,355				2,700	2.86			5	46.60	17	163
1928	420	5.43	350	2,200							217	458	1,605				2,785	2.68			5		18	146
1929	410	5.53	381	2,000					0.6	6.78	318	634	1,564				3,172	2.55			6		24	145
1930	370	5.72	410	1,800					0.3	5.62	327	550	1,360				2,571	2.38			2		17	
1931	221	5.20	306	1,147					0.8	4.21	213	378	922				1,475	2.54					9	
1932	109	5.10	206	1,003					0.2	9.81	89	300	472				726	2.83					7	sv
1933	174	5.37	150	1,098		30-40			1.1	10.50	117		884				1,134	2.77		1,000			8	122
1934	179	6.40	167	1,315													1,229	3.03		1,200			14	
1935	262	5.95	200	1,600					0.6	10.85	259	780	455	8.25			1,938	2.64		1,500			18	
1936	417	5.28	323	394		30	0.2		0.3	9.87	324	1,051	597	8.18			2,471	2.48		2,000	1	140.00	24	sv
1937	114	4.00	507	777			0.2		2.2	6.00	534	1,260	618	8.45	9		2,785	2.60		2,300	2	107.00	30	134
1938	87	3.62	456	903				1	0.9	12.00	352	1,107	367	8.45	3		1,459	2.78		1,200	1	115.00	18	140
1939	114	3.48	520	1,268	0.095	28.63		1	4.4	11.80	318	1,163	672	8.10	0.2		2,229	2.60		1,500	1	113.00	23	175
1940	571	3.10	630	4,459	0.121	30.75		2	3.3	8.52	737	1,458	867	8.00			2,765	2.55		2,300	2	91.00	31	120
1941	1,215	3.85	1,117	5,911	0.158	46.20	2	4	15.4	17.80	1,115	1,835	1,069	8.50	0.1		4,168	2.24		3,600	3	74.80	41	110
1942	2,910	4.63	844	8,424	0.269	89.92	2	3	123	20.43	980	1,973	1,229	8.85	0.5		4,839	2.35		4,300	7	55.30	44	125
1943	6,980	4.43	1,547	14,169	0.356	124.74	5	5	176	27.20	928	1,761	1,276	8.80	0.7		7,798	2.20			10	94.20	29	100
1944	3,160	4.57	560	7,476	0.388	144.67	3	3	49.5	28.90	848		1,290	8.88			6,344	2.23			5	60.50	26	80
1945	1,090	5.13	739	3,926	0.039	157.26	1	1	15.4	34.60	914		1,187	8.95	0.1		6,090	2.56			5	54.00	36	40

TABLE 19. NATURAL MINERALS

Material	Formula	Fusion point (pure)	Occurrence	Specific gravity	Hardness
Allophane	$Al_2SiO_5 \cdot nH_2O$		Few deposits	1.88–1.94	3
Alumian	$Al_2O_3 \cdot 2SO_3$ (perhaps)		Very rare	2.70–2.78	2–3
Aluminite	$Al_2O_3 \cdot SO_3 \cdot 9H_2O$		Not common	1.66	1–2
Alunite	$K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$		Commercial deposits	2.63–2.73	3.5–4
Alunogen	$Al_2O_3 \cdot 3SO_3 \cdot 16H_2O$		Rare	1.72–1.74	1.5–2
Amesite	$(Mg,Fe)_4 \cdot Al_2 \cdot Si_2 \cdot O_{10}(OH)_8$		Very rare	2.77	2.5–3
Anauxite	$Al_8(Si_4O_{10})_3(OH)_{12} \cdot 3H_2O$		Uncommon	2.59	2.5
Ancylite	$2Ce_2O_3 \cdot 3SrO \cdot 7CO_2 \cdot 5H_2O$		Very rare	3.82	4.5
Andalusite	Al_2SiO_5	1816°C. (3301°F.)	A few workable deposits	3.12–3.29	7.5
Ankerite	$(Ca,Mg,Fe)CO_3$		Occurs with dolomite	2.99–3.19	3.5–4
Apjohnite	$MnO \cdot Al_2O_3 \cdot 4SO_3 \cdot 22 \pm H_2O$		Very rare	1.78	1.5
Aragonite	$CaCO_3$	2570°C. (4658°F.)	Uncommon	2.86–3.15	3.5–4.0
Augelite	$2Al_2O_3 \cdot P_2O_5 \cdot 3H_2O$		Very rare	2.77	4.5–5
Aurichalcite	$5(Zn,Cu)O \cdot 2CO_2 \cdot 3H_2O$		Uncommon	3.27–3.64	2
Baddeleyite	ZrO_2	2700°C. (4892°F.)	Few deposits	5.5–6.03	6.5
Barite	$BaSO_4$	1580°C. (2876°F.)	Commercial deposits	4.62	2.5–3.5
Barylite	$BaBe_2Si_2O_7$		Very rare	4.03	7
Beckelite	$Ca_3(Ce,La,Di)_4Si_3O_{15}$		Very rare	4.15	5
Beidellite	$Al_8(Si_4O_{10})_3(OH)_{12} \cdot 12H_2O$		Widespread		
Bertrandite	$Be_4Si_2O_7(OH)_2$		Rare	2.59–2.60	6–7
Beryl	$Al_2Be_3Si_6O_{18}$	1410–1430°C. (2570–2606°F.)	Commercial deposits	2.55–2.91	7.5–8
Brookite	TiO_2	1900°C. (3451°F.)	Rare	3.97	5.5–6.0

Brucite	$Mg(OH)_2$	2800°C. (5072°F.)	Commercial deposits rare	2.38–2.39	**2.5**
Bunsenite	NiO		Very rare	6.40	**5.5**
Calcite	$CaCO_3$	2570°C. (4658°F.)	Commercial deposits	2.70–2.82	**3.0**
Cassiterite	SnO_2		Commercial deposits (not in U.S.A.)	6.72–6.91	**6–7**
Celsian	$BaAl_2Si_2O_8$		Very rare	3.3–3.45	**6–6.5**
Cerite	$(Ce,Y,Pr,Nd)_2Si_2O_7 \cdot H_2O$		Very rare	4.86–4.91	**5.5**
Chalcedony	SiO_2	1715°C. (3119°F.)	Commercial deposits	2.55–2.63	**6**
Chalcophanite	$(Mn,Zn)O \cdot 2MnO_2 \cdot 2H_2O$		Rare	3.91	**2.5**
Chondrodite	$Mg_5(SiO_4)_2(OH,F)_2$		Rare	3.18	**6–6.5**
Chromite	$FeCr_2O_4$	2180°C. (3956°F.)	Numerous workable deposits	4.32–4.57	**5.5**
Chrysoberyl	$BeAl_2O_4$		Commercial deposits rare	3.49–3.73	**8.5**
Chrysocolla	$CuSiO_3 \cdot 2H_2O$		Uncommon	2.40–2.42	**2–4**
Churchite	$(Ce,Ca)PO_4 \cdot 2H_2O$		Very rare	3.14	**3–3.5**
Clinoenstatite	$Mg_2Si_2O_6$		Rare	3.19	**6**
Clinohumite	$Mg_9(SiO_4)_4(OH,F)_2$		Rare	3.1–3.21	**6.0–6.5**
Columbite	$(Fe,Mn)(Nb,Ta)_2O_6$		Uncommon	5.15–6.85	**6**
Cordierite	$(Mg,Fe,Mn)_2(Al,Fe)_4Si_5O_{18} \cdot H_2O$			2.57–2.66	**7–7.5**
Corundum	Al_2O_3	2050°C. (3722°F.)	Commercial deposits	3.97–4.03	**9**
Cristobalite	SiO_2	1715°C. (3200°F.)	Very rare	2.32–2.36	**6–7**
Derbylite	$6FeO \cdot Sb_2O_3 \cdot 5TiO_2$		Very rare	4.51–4.53	**5**
Diamond	C		Very rare	3.20–3.51	**10**
Diaspore	AlO(OH)	2035°C. (3695°F.)	Many deposits	3.39	**6.5–7**
Dickite	$Al_2Si_2O_5(OH)_4$	1785°C. (3245°F.)	In some clays; uncommon	2.62	**2.5**
Dioptase	H_2CuSiO_4		Very rare	3.30–3.32	**5**
Dolomite	$CaMg(CO_3)_2$	2570–2800°C. (4658–5072°F.)	Commercial deposits	2.83–2.99	**3.5–4.3**

TABLE 19. NATURAL MINERALS (*Continued*)

Material	Formula	Fusion point (pure)	Occurrence	Specific gravity	Hardness
Dumortierite	$AlB_3Si_2O_{19}(OH)$		Very rare	3.30–3.36	7
Dysanalyte	$7(Ca,Ce,Fe,Na_2)O{\cdot}6TiO_2{\cdot}Cb_2O_5$		Very rare	4.26	5–6
Euxenite	Columbate and titanite of Y, Er, Ce, U, etc.		Very rare	4.59–4.99	6.5
Evansite	$2AlPO_4{\cdot}4Al(OH)_3{\cdot}12H_2O$		Very rare	1.92–1.93	3.5–4
Fergusonite	$Y(Nb,Ta)O_4$		Very rare	4.98–5.78	5.5–6
Fermorite	$(Ca,Sr)_4[Ca(OH,F)][(P,As)O_4]_3$		Rare	3.52	5
Fluellite	$AlF_2{\cdot}H_2O$		Very rare	2.17	3
Fluocerite	$(Ce,La,Di)F_3$		Very rare	5.73	4
Forsterite	Mg_2SiO_4	1910°C. (3470°F.)	Uncommon	3.22–3.27	6–7
Franklinite	$(Zn,Fe,Mn)(Fe,Mn)_2O_4$		Uncommon	5.09	5.5–6.5
Gadolinite	$(Al,Fe''',Ti)_2Fe''Be_2(SiO_4)_2O_2$		Very rare	4.0–4.6	6.5–7.0
Gahnite	$ZnAl_2O_4$		Rare	4.48–4.60	7.5–8.0
Garnierite	Perhaps $H_2(Ni,Mg)SiO_4 + H_2O$ very variable		Widespread	2.27–2.87	1–3
Geikielite	$(Mg,Fe)TiO_3$		Rare	3.98–4	6
Gibbsite (hydrargillite)	$Al(OH)_3$	2035°C. (3695°F.)	Common	2.3–2.42	2.5–3.5
Goethite	$HFeO_2$		Widespread	4.18–4.48	5 0–5.5
Goslarite	$ZnSO_4{\cdot}7H_2O$		Rare	1.9–2.1	2–2.5
Grandidierite	$2Na_2O{\cdot}4FeO{\cdot}8(Fe,Al,B)_2O_3{\cdot}5SiO_2$		Very rare	2.99	7.5
Graphite	C		A few deposits	2.22	1–2
Greenockite	CdS		Rare	4.82	3–3.5
Grothine	Silicate of Ca, Al, Fe (uncertain)		Very rare	3.08–3.09	
Gummite	Doubtful composition, alternative product of uraninite		Rare	5.08	2.5–3
Halloysite	$Al_4Si_4O_{10}(OH)_8{\cdot}H_2O$	1775°C. (3227°F.)	A few deposits	2.44–2.71	1–2

Hambergite	$Be_2BO_3(OH)$		Rare	≥.36	7.5
Hatchettolite	Tantalocolumbate of U, Ca, etc.		Very rare	4.42–4.51	5
Hausmanite	Mn_3O_4		Uncommon	4.78–4.84	5–5.5
Hematite	Fe_2O_3		Common	5.17–5.26	5–6.5
Hematolite	$8MnO\cdot(Al,Mn)_2O_3\cdot As_2O_5\cdot 8H_2O$		Very rare	3.30–3.40	3.5
Hercynite	$FeAl_2O_4$		Rare	4.01	7.5–8.0
Hinsdalite	$2PbO\cdot 3Al_2O_3\cdot 2SO_3\cdot P_2O_5\cdot 6H_2O$		Rare	3.65	4.5
Hisingerite	$Fe_2O_3, MgO, FeO, SiO_2, H_2O$, etc.		Rare	2.50	3–3.5
Högbomite	$MgO\cdot 2(Al,Fe)_2O_3$, some TiO_2		Rare	3.81	6.5
Humite	$Mg_7(SiO_4)_3(OH,F)_2$		Rare	3.1–3.2	6–6.5
Hydromagnesite	$4MgO\cdot 3CO_2\cdot 4H_2O$		Uncommon	2.15–2.16	3.5
Hydrotalcite	$6MgO\cdot Al_2O_3\cdot CO_2\cdot 12H_2O$		Rare	2.04–2.09	2
Hydrozincite	$7ZnO\cdot 3CO_2\cdot 4H_2O$		Uncommon	3.58–3.8	2.0–2.5
Iddingsite	$MgO\cdot Fe_2O_3\cdot 3SiO_2\cdot 4H_2O$		Widespread	2.54–2.80	2.5–3
Ilmenite	$FeTiO_3$		Common	4.44–4.86	5–6
Incobsite	$MnFe_2O_4$		Uncommon	4.75–4.76	6
Kaliophilite	$(K,Na)(Al.Si)_2O_4$		Uncommon	2.56–2.61	6
Kaolinite	$Al_2Si_2O_5(OH)_4$	1785°C. (3245°F.)	Common in clays	2.6–2.63	2.0–2.5
Kehoeite	$3(Zn,Ca)O\cdot 2Al_2O_3\cdot P_2O_5\cdot 27 \pm H_2O$		Very rare	2.34	
Koppite	$2(Ca,Ce,\text{etc.})O\cdot Cb_2O_5\cdot \frac{1}{3}NaF$		Rare	4.45–4.56	5.5
Kornerupine	Near $MgAl_2SiO_5$		Very rare	3.27–3.34	6.5
Kreittonite	$(Zn\cdot Fe)(Al\cdot Fe)_2O_4$		Uncommon	4.48–4.89	7–8
Kyanite	Al_2SiO_5		Small deposits	3.28–3.59	4–7
Langbanite	$Sb_2O_3, Fe_2O_3, Mn_2O_3, SiO_2$		Very rare	4.6–4.8	6.5
Lansfordite	$MgO\cdot CO_2\cdot 5H_2O$		Very rare	1.69–1.73	2.5
Lazulite	$AlPO_4(Fe,Mg)(OH)_2$		Rare	2.96	5–6
Limonite	$Fe_2O_3\cdot nH_2O$		Common	3.87	4–5.5
Mackintoshite	$(U,Ce,Th,La,Y,Pb)_2SiO_5$		Very rare	5.44	5.5
Magnesioferrite	$MgFe_2O_4$		Rare	4.57–4.65	6.0–6.5
Magnesite	$MgCO_3$	2800°C. (5072°F.)	Commercial deposits	2.95–3.12	3.5–4.5
Manganite	$Mn(OH)O$		Uncommon	4 29	4–5
Manganosite	MnO		Very rare	5 36	5–6
Martinite	$H_2Ca_5(PO_4)_4\cdot \frac{1}{2}H_2O$		Very rare	2.89	

TABLE 19. NATURAL MINERALS (*Continued*)

Material	Formula	Fusion point (pure)	Occurrence	Specific gravity	Hardness
Melanocerite	$Ca_{16}Na_4(Y,La)_3(Zr,Ce)6Be_2Si_{12}O_{47}F_{12}$		Very rare	4.13	5–6
Mesitite	$(Fe,Mg)CO_3$		Widely distributed	3.38	
Metavansite	$Al_2O_3{\cdot}P_2O_5{\cdot}4H_2O$	>1500°C. (>2732°F.)	Rare	2.54	4
Microlite	Essentially $Ca_2Ta_2O_7$		Very rare	5.41–5.56	5.5
Miloschite	$(Al,Cr)_2O_3{\cdot}2SiO_2{\cdot}2H_2O$		Very rare	2.13	1.5–2.5
Moissanite (natural) (silicon carbide synthetic).	SiC	2500°C. (4532°F.)	Unique	3.2	9.5
Molybdenite	MoS_2		A few extensive commercial deposits	4.62	1–1.5
Monazite	$(La,Ce,Y)PO_4$		A few deposits	5.11–5.31	5–5.5
Montmorillonite	$(OH)_2Al_2[Si_2O_5]_2{\cdot}nH_2O$		Common	2.04–2.52	Soft
Morenosite	$NiSO_4{\cdot}7H_2O$		Fairly rare	2.00	2.0–2.5
Nacrite	$Al_2Si_2O_5(OH)_4$	1785°C. (3245°F.)	Very rare	2.5+	2.5
Nephelite	$(Na,K)(Al,Si)_2O_4$	1526°C. (2779°F.)		2.53–2.66	5.5–6
Nontronite	Member of beidellite group		Uncommon	2.29–2.30	
Norbergite	$Mg_3(SiO_4)(OH,F)_2$		Rare	3.13–3.15	6.5
Octahedrite	TiO_2	1900°C. (3452°F.)	Rare	3.95	5.5–6
Olivine	$(Mg,Fe)SiO_4$	1700–1910°C. (3092–3470°F.)	Common	3.2–3.3	6.5–7
Opal	$SiO_2{\cdot}nH_2O$	1715°C. (3119°F.)	A few deposits	2.06–2.22	5.5–6.5
Parisite	$2(Ce,La,Di,Th)OF{\cdot}CaO{\cdot}3CO_2$		Rare	4.32	4.5
Periclase	MgO	2800°C. (5072°F.)	Rare	3.64–3.67	5.5–6

Perovskite	$CaTiO_3$		Commercial deposits unknown	3.95–4.04	5.5
Phenacite	Be_2SiO_4	2000°C. (3632°F.)	Rare	2.94–3.04	7.5–8
Picotite	$(Mg,Fe)(AlCr)_2O_4$		Rare	4.08	
Pigeonite	$(Ca,Mg)(Mg,Fe)Si_2O_6$		Widespread	3.2–3.4	6
Polianite	MnO_2		Rare	4.84–5.03	6–6.5
Polycrase	Columbate and titanate of Y, U, Th, Fe, etc.		Rare	4.97–5.04	5–6
Polymignite	Columbate, titanate, zirconate of Ce, etc.		Very rare	4.77–4.85	6.5
Prosopite	$CaF_2 \cdot 2Al(F,OH)_3 \cdot H_2O$		Rare	2.88–2.89	4.5
Pseudobrookite	Fe_2TiO_5		Rare	4.60	6
Pyroaurite	$6MgO \cdot Fe_2O_3 \cdot CO_2 \cdot 12H_2O$		Rare	2.07	2–3
Pyrochlore	Columbate and titanate of Ce, Ca, etc. with Th, F, etc.		Very rare	4.2–4.36	5–5.5
Pyrolusite	MnO_2		Uncommon	4.75–4.89	2.0–2.5
Pyrope	$Mg_3Al_2(SiO_4)_3$		Uncommon	3.51–3.75	7.0–7.5
Pyrophanite	$MnO \cdot TiO_2$		Very rare	4.54	5
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$		Rare	2.66	1–3
Quartz	SiO_2	1715°C. (3119°F.)	Very plentiful	2.65–2.70	7
Ralstonite	$(Na_2,Mg)F_2 \cdot 3Al(F,OH)_3 \cdot 2H_2O$		Very rare	2 61	4.5
Retzian	Arsenate of Y, Mn, Ca, etc., and H_2O		Very rare	4.15	4
Rhabdophanite	$(Y,Er,La,Di)_2O_3 \cdot P_2O_5 \cdot 2H_2O$		Very rare	3.94–4.01	3.5
Rhodochrosite	$MnCO_3$		Small deposits	3 31–3.74	3.5–4.5
Rhodolite	$3(Mg,Fe)O \cdot Al_2O_3 \cdot 3SiO_2$		Rare	3.75–3.84	7–7.5
Risörite	$Cb_2O_5(Y,Er)_2O_3 \cdot H_2O$, some Ta, Ti, Ce, La, etc.	1720°C. (3128°F.)	Very rare	4.18	5.5
Rosieresite	Hydrous phosphate of Al, Pb and Cu		Very rare	2.2	
Rowlandite	$(Y,Ce,La)_4Fe''(Si_2O_7)_2 \cdot F_2$		Very rare	4.52	6–7
Rutile	TiO_2	1900°C. (3452°F.)	Few large deposits but widely distributed	4.12–4.27	6.0–6.5
Saponite	$(Mg,Fe'')_{2.28}(Al,Fe''')_{.72}Si_{3.64}O_{10}(OH)_{2.28} \cdot 4H_2O$			2.18–2.31	Soft
Sapphirine	$Mg_4Al_{12}Si_2O_{27}$		Rare	3.3–3.5	7.5

TABLE 19. NATURAL MINERALS (*Continued*)

Material	Formula	Fusion point (pure)	Occurrence	Specific gravity	Hardness
Schneebergite	$2CaO \cdot Sb_2O_4$		Rare	5.41	6.5
Schroetterite	$3Al_2O_3 \cdot SiO_2 \cdot nH_2O$		Rare	1.95–2.05	3–3.5
Sillimanite	Al_2SiO_5	1816°C. (3300°F.)	A few commercial deposits	3.23–3.24	6–7.5
Sipylite	Columbate of Er, La, Di, U, etc.		Very rare	4.89	6
Smithsonite	$ZnCO_3$		Widespread	4.19–4.41	4.5–5
Sphaerocobaltite	$CoCO_3$		Rare	4.02–4.13	3–4
Spinel	$MgAl_2O_4$	2135°C. (3875°F.)	Small deposits	3.68–3.92	8
Spurrite	$5CaO \cdot CO_2 \cdot 2SiO_2$		Rare	3.01	5
Stibiconite	$Sb_2O_4 \cdot nH_2O$		Rare	5.1–5.3	4–5
Stichtite	$6MgO \cdot Cr_2O_3 \cdot CO_2 \cdot 12H_2O$		Rare	2.16	1.75
Symplesite	$3FeO \cdot As_2O_5 \cdot 8H_2O$		Very rare	2.96	2.5
Szmikite	$MnO \cdot SO_3 \cdot H_2O$		Very rare	3.15	1.5
Tantalite	$(Fe,Mn)O \cdot (Ta,Cb)_2O_5$			6.5–8.20	6
Tapiolite	$FeO \cdot (Ta,Cb)_2O_5$		Very rare	7.19–7.91	6
Tavistockite	$3CaO \cdot Al_2O_3 \cdot P_2O_5 \cdot 2H_2O$		Very rare		
Thalenite	$(Al,Fe''',Ti)_2Si_2O_7$		Very rare	4.45	6.5
Thaumasite	$3CaO \cdot CO_2 \cdot SO_3 \cdot SiO_2 \cdot 15H_2O$		Rare	1.85–1.88	3.5
Thorianite	Chiefly $(Th,U)O_2$	1660°C. (3020°F.)	Very rare	9.33	6.5
Thorite	$ThSiO_4$		Rare	5.2–5.4	4.5–5.0
Topaz	$Al_2SiO_4(F,OH)_2$		Commercial deposits scarce	3.35–3.59	8
Tridymite	SiO_2		Rare	2.28–2.33	7
Tungstite	$WO_3 \cdot H_2O$		Rare	5.5	2.5
Turquoise	$CuO \cdot 3Al_2O_3 \cdot 2P_2O_5 \cdot 9H_2O$		Rare	2.84	5
Uraninite	A uranate of U, Pb, Th, Zr, and metals of La and Y groups		Rare	7.13–9.79	5.5

TABLE 19. NATURAL MINERALS (*Continued*)

Material	Formula	Fusion point (pure)	Occurrence	Specific gravity	Hardness
Uranophane	$CaU_2Si_2O_{11}\cdot 7H_2O$		Rare	3.81–3.96	2–3
Uranothallite	$2CaO\cdot UO_2\cdot 4CO_2\cdot 10H_2O$		Rare		2.5–3
Uvarovite	$Ca_3Cr_2(SiO_4)_3$		Rare	3.42–3.81	6.5–7.5
Variscite	$Al_2O_3\cdot P_2O_5\cdot 4H_2O$		Rare	2.47	4
Vashegyite	$3Al_2O_3\cdot 2P_2O_5\cdot 18 \pm H_2O$ (about)		Rare	1.96	2–3
Voelckerite	$10CaO\cdot 3P_2O_5\cdot P_2O_5$	1540°C. (2804°F.)	Not common	3.06–3.10	
Volchonskoite	$(Al,Fe''',Cr)_4(Si_4O_{10})(OH)_8$		Rare	2.2–2.3	2.5
Voltzite	$ZnO\cdot 4ZnS$		Very rare	3.66–3.80	4.0–4.5
Wavellite	$3Al_2O_3\cdot 2P_2O_5\cdot 13(H_2O\cdot 2HF)$		Uncommon	2.33	3.5–4.0
Whewellite	$CaO\cdot C_2O_3\cdot H_2O$		Rare	2.23	2.5
Wiikite	Columbate, titanate, and silicate of Fe and rare earths		Very rare	3.8–4.8	6
Willemite	Zn_2SiO_4		Uncommon	3.89–4.19	5.5
Xenotime	YPO_4		Uncommon	4.55	4–5
Yttrialite	$(Y,Th)_2O_3\cdot 2SiO_2$		Very rare	4.58	5–5.5
Yttrocrasite	Hydrous titanate of Th, Y, etc.		Rare	4.80	5.5–6
Zebedassite	$5MgO\cdot Al_2O_3\cdot 6SiO_2\cdot 4H_2O$		Very rare	2.19	2
Zepharovichite	$Al_2O_3\cdot P_2O_5\cdot 6H_2O$	>1500°C. (>2732°F.)	Very rare	2.37	5.5
Zincaluminite	$6ZnO\cdot 3Al_2O_3\cdot 2SO_3\cdot 18H_2O$		Very rare	2.26	2.5–3.0
Zincite	ZnO		Rare	5.43–5.7	4.0–4.5
Zircon	$ZrSiO_4$	2550°C. (4622°F.)	Few deposits	4.05–4.75	7.5
Zirkelite	$(Ce,Fe,Ca)O\cdot 2(Zr,Ti,Th)O_2$		Very rare	4.3–5.22	5.5
Zunyite	$Al_4(SiO_4)_3(F,Cl,OH)_{12}$		Very rare	2.88	7

CHAPTER V

THE MINING AND PRELIMINARY TREATMENT OF REFRACTORY MATERIALS

1. Mining of Clays. *Open-pit Methods.* Many refractory clays are mined by open-pit methods. Usually the bed of clay is covered by an overburden of gravel or earth, which may run as thick as 10 to 20 ft. If

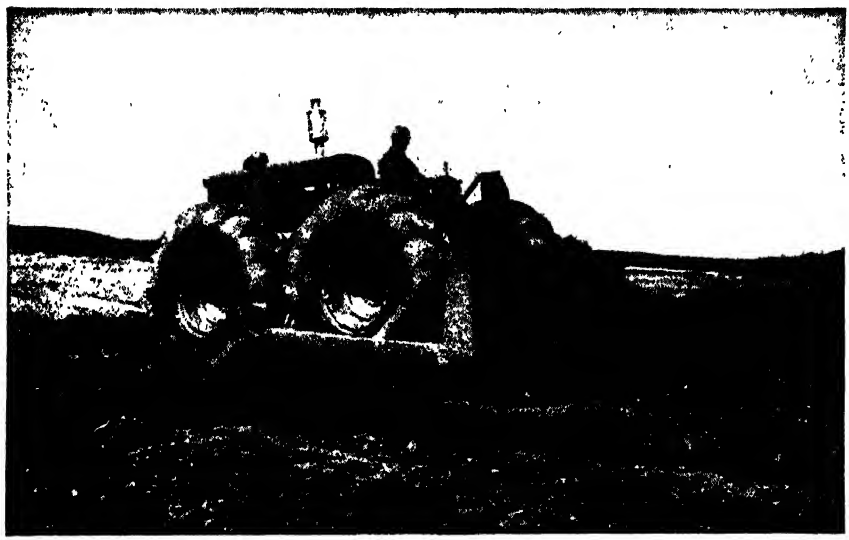


FIG. 21. A rubber-tired bulldozer for clay stripping. (*Courtesy of the Le Tourneau Company.*)

the thickness of overburden is much greater than 20 ft, it is seldom economical to mine a low-cost clay by this method.

The first process consists in stripping off the overburden in the most economical manner. In small workings where the overburden is thin, this was done by horse-drawn scrapers; but in larger operations, the overburden is stripped by power shovels, tractor-pulled wheel scrapers, bulldozers, or shovel dozers. In other workings, it is found economical to strip the overburden with dragline scrapers with a capacity of ⅓ to 4 cu yd. This type of scraper is very flexible and can be made to cover a large area by using a movable cable anchor. Lines as long as 500 ft are used; and with a 1 cu yd bucket, 20 to 75 cu yd per hr can be moved, depending upon the length of the haul. A modern bulldozer for stripping

the overburden from a kaolin deposit is shown in Fig. 21, and in Fig. 22 is shown a self-powered scraper of large capacity.

The method of removing the clay itself varies with the conditions. If the clay is fairly soft, the face can be broken with picks or bars and the broken material loaded by hand into carts or cars. In the larger plants, however, this method is not economical, and power shovels are generally used. The shovel capacity varies from ½ to 2 cu yd. The larger shovels are chosen not only for their greater capacity but also for their greater strength and longer reach. Caterpillar treads are almost universally used. A 1 cu yd shovel will load, under good conditions, 500 tons of clay in an 8-hr day. Recently, lighter and more agile shovels are being favored.

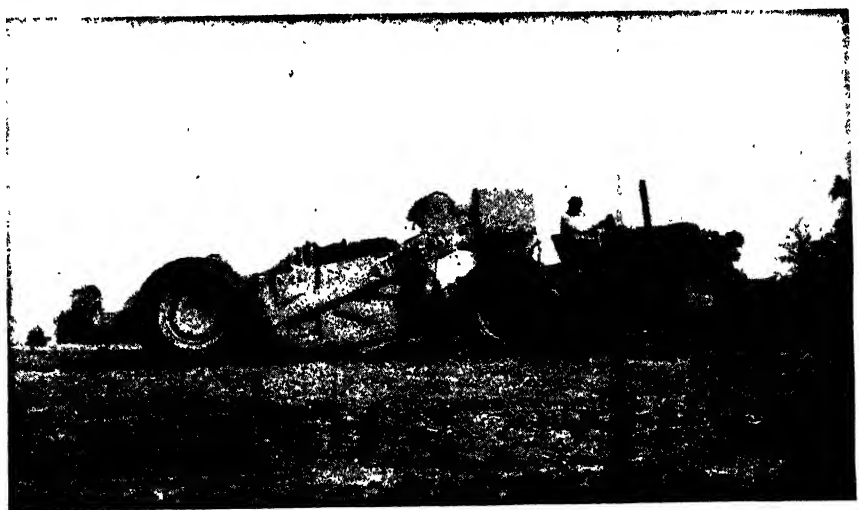


FIG. 22. A self-powered scraper for stripping clay. (*Courtesy of the Le Tourneau Company.*)

The softer clays can be taken out with dragline scrapers or bucket excavators. Often wheel scrapers are used, as shown in Fig. 23.

Provided the clay is not too hard and yet is firm enough to hold a permanent face, as in the case of many shales, it has been found economical to remove the materials by a planer, which is an endless chain with cutting knives working vertically on the whole face as shown in Fig. 24. This machine has the advantage of removing the material in small pieces and of giving a good average composition by taking the material from the whole face. The cost of removing the material with a machine of this type is comparatively low, as one man can usually operate it and obtain a production of 200 to 400 tons a day.

In Europe, the endless-chain excavator working from the top of the bank is often used. Although the initial investment is large, the low

FIG. 23. Mining clay with a Caterpillar tractor and scraper. (*Courtesy of the Allis-Chalmers Manufacturing Company.*)

labor and maintenance cost justifies it on large operations. One man can remove 100 tons per hr with an average-sized machine.

In the case of hard clay, it is generally necessary to drill and blast the face in order to obtain small enough pieces to be readily handled. The

FIG. 24. Removing kaolin with a shale planer made by the Eagle Iron Works at the Georgia Kaolin Company. (*Courtesy of the Georgia Kaolin Company.*)

drilling is done in the smaller pits with hand drills of 1 to 1½ in. in diameter. In the larger mines, however, electric and air drills are used. Recently, portable well drills have been used to a considerable extent to drill deep holes behind the working face so that larger and deeper charges of explosives can be set off. These drills will produce holes from 3 to 5½ in. in diameter, which will allow the use of a considerable quantity of explosive.

When the clay has been loosened from the face, it is loaded into cars or trucks by hand or power shovels as shown in Fig. 25.

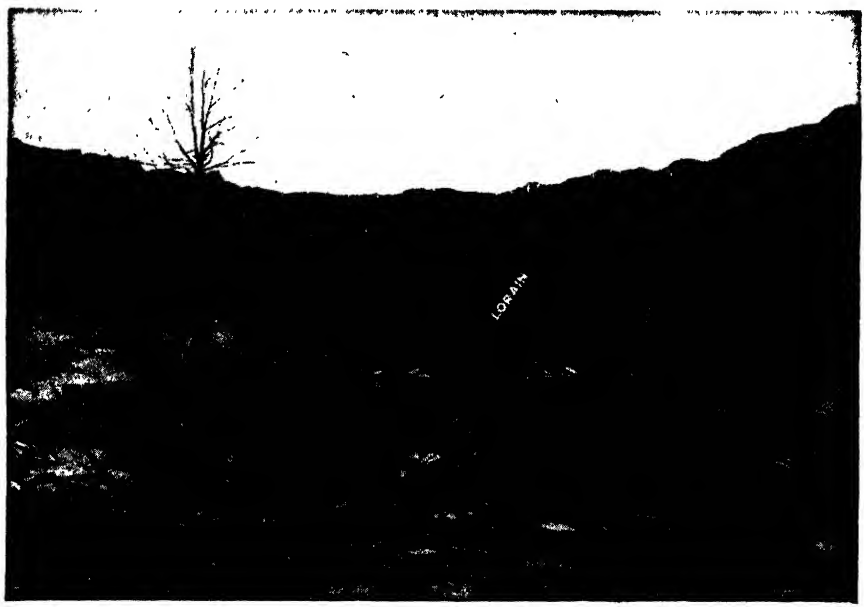


FIG. 25. Mining with a power shovel. (*Courtesy of The Thew Shovel Company.*)

Underground Methods. When the clay deposit is too deep for stripping, underground mining is used. Most of the productive clay veins are from 5 to 15 ft thick. The room-and-pillar method is generally used, with advance from the entrance, which consists of cutting a mine entry and advancing galleries from that out to the edge of the property. This method has the advantage of not requiring extensive entry development when the mine is started, but it is not so economical as the retreating method, which consists of cutting an entry to the boundary line and then starting the galleries at the farther end. Work is then carried toward the entrance. The pillars can be drawn only where the subsidence of the ground is unimportant. Whenever underground mining is used, it is

important to plan out the workings carefully and have a systematic method before starting to mine.

Practically all underground clay is taken out by drilling and blasting. Hand, electric, or pneumatic drills are used, and the lumps of clay are loaded on the car by hand or, in more modern mines, by car loaders.

The same factors of economical mining apply to clay mines as to other mines. In the first place, drainage must be well cared for, as muddy

FIG. 26. A tractor loader filling a dump car. (*Courtesy of the Oliver Tractor Company.*)

floors and tracks increase the haulage costs as well as make the timbering difficult. Next, the timbering should be well done with generous posts. The tracks should also be graded and kept in good condition, as the haulage cost mounts up when dirty, poorly laid tracks are used.

Clay is usually transferred to the plant on rails with dump cars ranging in capacity from ½ to 6 cu yd (Fig. 26). The cars are propelled by steam, oil, or gasoline locomotives or sometimes by cable haulage. In a few cases where the distance from the mines to the plant is considerable and the country is rough, it has been found economical to transfer the clay by aerial cableways. Trucks are coming into more general use than formerly.

It is hard to give any definite figures on the cost of mining clay; but in

general, clay can be loaded on cars or trucks from the open pit under the best conditions for 50 cents a ton. Where the overburden is heavy or where hand selection is used, the cost may run as high as $1 per ton at the plant. In the case of special high-grade clays, the cost may run even higher. It may be said, however, that a great number of plants are getting out their refractory clays for around 50 cents per ton. In underground mining, the cost varies according to the thickness of the vein, the hardness of the clay, the amount of timbering required, and the distance to the plant—the variation in most cases being from $1.50 to $2.50 per ton on

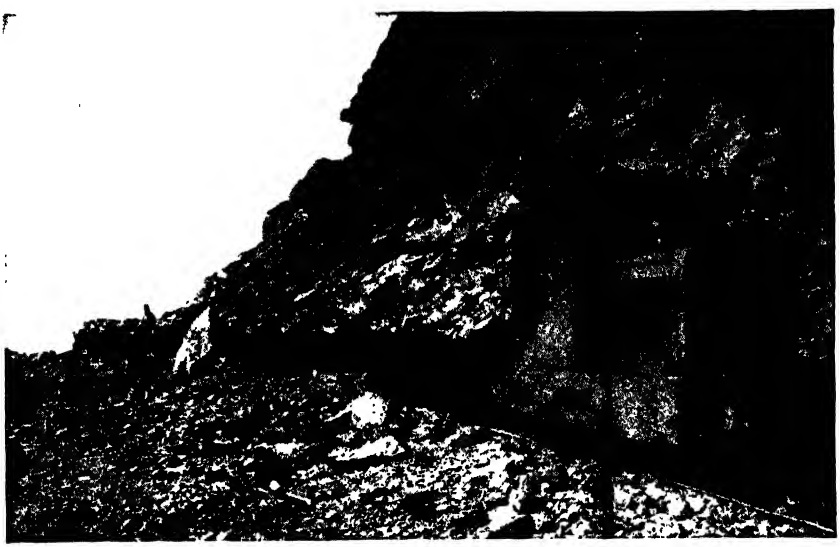


FIG. 27. Mining ganister rock. (*Courtesy of the Harbison-Walker Refractories Company.*)

cars. It may be mentioned that in many of the underground clay mines, coal is obtained at the same time as clay, which, of course, reduces the total cost considerably.

2. The Mining of Ganister. Since the mining of ganister is rather different from clay mining, it will be described separately. The ganister is usually found in flows of loose rock on the mountain sides (Fig. 27). Where the rocks are large, they are broken up by mud capping and blasting; in only a few cases is drilling necessary. The smaller rocks are broken up by sledges into sizes that can be lifted by hand. The broken rock is loaded into dump cars by hand, as some sorting is necessary. One man will load from 15 to 20 tons of rock a day.

The dump cars are trammed either by hand or by locomotive, as the case may be, to a gravity plane and dumped into cars to be lowered down

the plane. In a few cases, ganister is carried long distances by railroad to reach the plant.

In some localities, the ganister is obtained from bedrock, because the flows have been used up or because the rock is more uniform. The ledge rock, however, is usually not thought to be so satisfactory as the flow rock, because the soluble constituents have not been leached out by weathering. Others claim that bedrock gives superior bricks. Regular quarrying methods are used in removing this rock from the hillside. This material will cost 75 cents to $1.50 a ton on cars.

3. Crushing and Grinding. Practically all clay must be crushed before it is taken to the tempering and brickmaking machinery. The

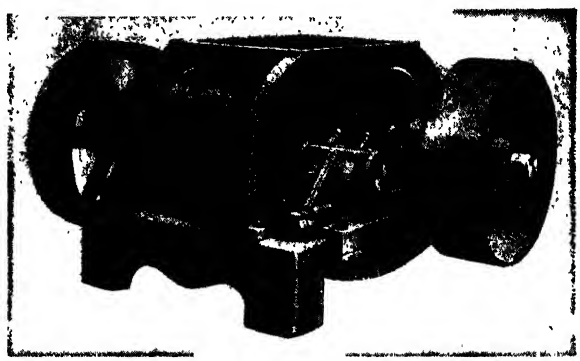


FIG. 28. A roll crusher. (*Courtesy of the W. A. Riddell Corporation.*)

softer lump clays are usually passed through single or double roll crushers, which rapidly break down the lumps to sizes small enough for wet pans or pug mills. The wear and tear on rolls of this type is very small, so the cost of breaking up the softer types of clays is not great.

Jaw or gyratory crushers are usually used for the harder clays, rocks, and grog. They will crush down to 1 in. with capacities of ½ to 500 tons an hour. These crushers cannot be used for the softer clays containing moisture because of packing in the jaws.

Roll crushers (Fig. 28) are used for crushing hard materials from 1 in. down to ¼ or ⅛ in. For materials like grog, the rolls should be supplied with tires of manganese steel, as the wear is considerable. In order to obtain fine grinding, it is necessary to keep the rolls fairly true cylinders, as flanges tend to form on the ends and the material will be passed through the center uncrushed. Plain rolls should never be used for crushing clays with any moisture, because the material builds up on the rolls and there will be no crushing action.

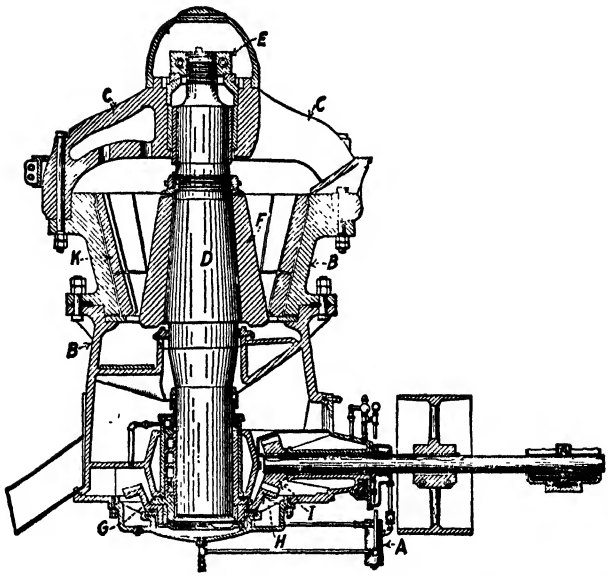


FIG. 29 Sectional view of a gyratory crusher. (*From C. E. Locke.*)

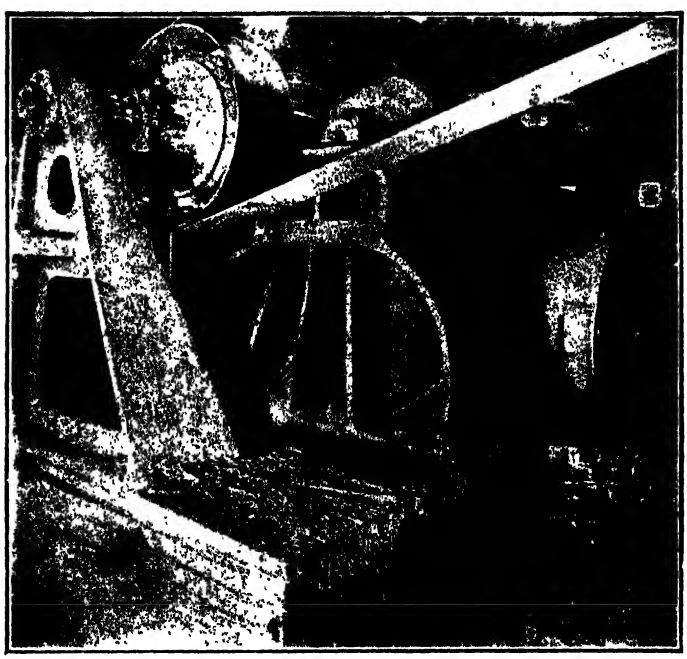


FIG. 30. A dry pan for crushing flint clay. (*Courtesy of Clearfield Machine Company.*)

Gyratory crushers (Fig. 29) are often used for crushing magnesite and ganister. These crushers have a large capacity but will not take such large rocks as jaw crushers.

Dry pans (Fig. 30) consist of a heavy revolving bed in a horizontal position on which the material is fed; two heavy rolls (mullers) rest on this bed with their own weight, crushing the material underneath. The portion of the bed not directly under the mullers is usually supplied with screens or slits so that crushed material can pass through, permitting con-

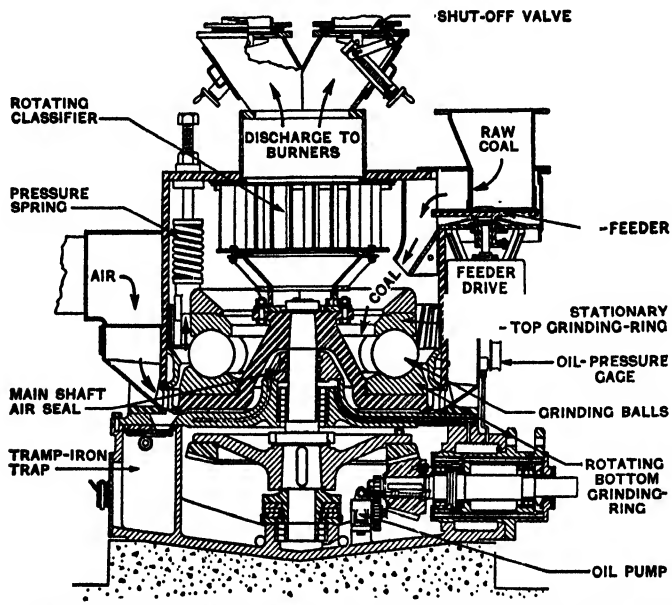


FIG. 31. Babcock and Wilcox pulverizer. (*Courtesy of Babcock and Wilcox Company.*)

tinuous operation. The dry pan is used for grinding flint clay, ganister, and burned grog. Wet pans are similar machines with a solid bottom so that the mix can be ground wet.

For finer grinding, it is often desirable to use crushers of the B and W, ring-roll, or hammer-mill type, as shown in Figs. 31, 32, and 33. Machines of these types will pulverize down to 100 or 150 mesh and can be used for clays with some degree of moisture.

Ball mills are much used for fine grinding. For large production, the continuous type of mill should be selected. The fine material is removed with an air separator, and the oversize is automatically returned to the mill. A production of several tons per hour of 200-mesh material can be obtained with this type of installation. Even when coarser material is

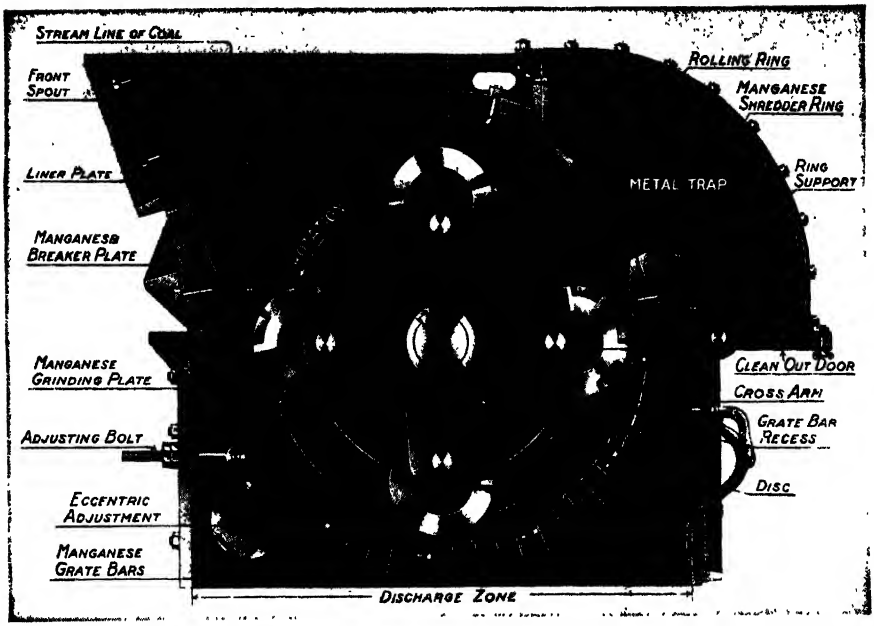


FIG. 32. Cross section of a ring roll crusher. (*Courtesy of the American Pulverizer Company.*)

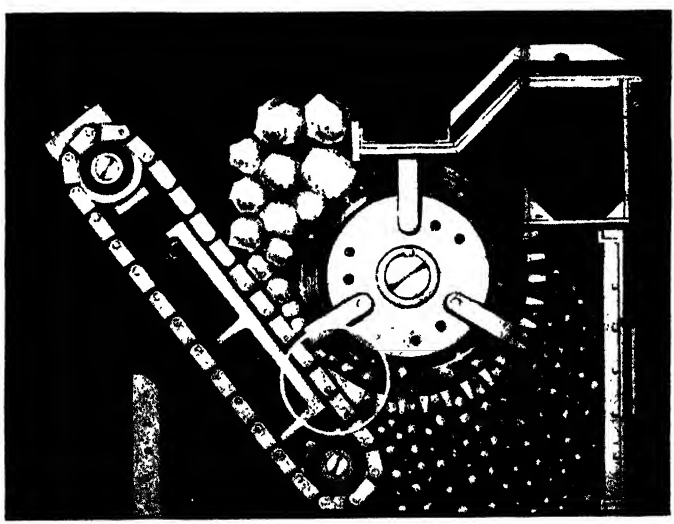


FIG. 33. Cross section of a hammer mill for fine grinding. (*Courtesy of Dixie Hammermill Manufacturing Company.*)

required, the continuous ball mill is often found suitable. In Fig. 34 is shown a typical closed-circuit, ball-mill installation for continuous grinding. The capacities of some ball mills are shown in Table 20. An interesting development in Germany[34] described by Dr. Ryschkewitsch is the

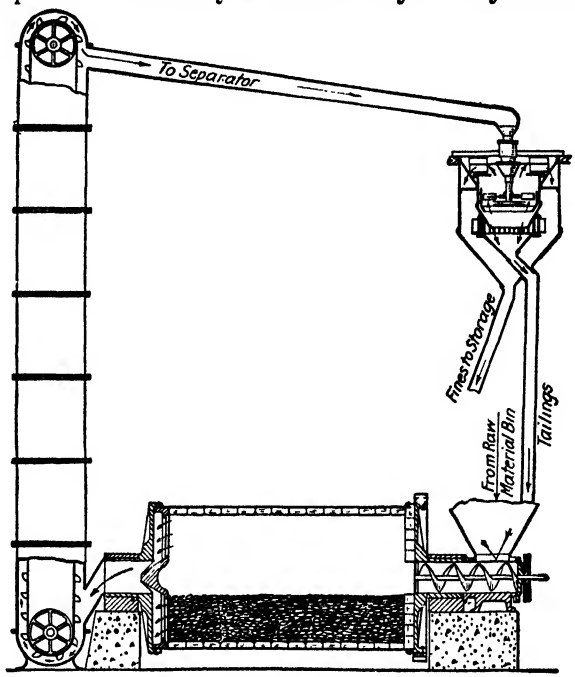


FIG. 34. Cross section of a continuous ball mill. (*Courtesy of Patterson Foundry and Machine Company.*)

vibrating ball mill. Here there is no rotation but a vibration of five per second, which causes the balls to flow around in a continuous motion. It is claimed that a 2 μ size can be reached by this method in the same time that 12 μ can be reached by conventional grinding.

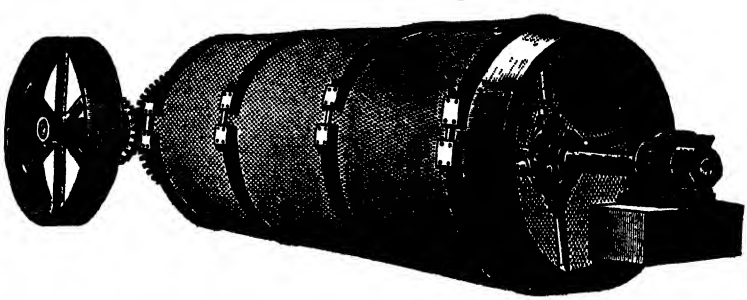


FIG. 35. A revolving screen for classifying coarse material. (*Courtesy of Gruendler Rock and Gravel Crushing Equipment Company.*)

4. Screening. It is usually necessary to screen the materials being crushed so that the required product can be passed on to the brickmaking machinery and the coarser material returned to the crushers. Various types of screens are used. A revolving screen or trommel is often used for classifying coarser materials (Fig. 35), and screens of several sizes can be

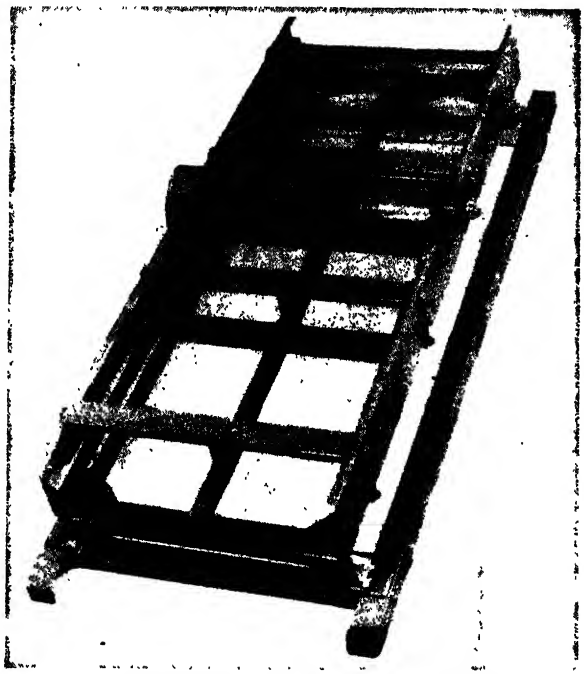


FIG. 36. An open-type shaking screen. (*Courtesy of the Universal Vibrating Screen Company.*)

TABLE 20
(From G. F. Metz)

Material	Size and type	Tons per hour	Circuit	Horse-power	Size of feed	Fineness of product	Pebble load, lb.
Silica (dry).....	7 × 22 ft. tube	3	Closed	210	−20 mesh	98 per cent minus 200 mesh	42,000
Sillimanite	3 × 2 ft. conical	¼	Closed	15	−¼-in. mesh	80 per cent minus 100 mesh	14,000
Grog	5 × 22 ft. conical	4½	Closed	40	−1½-in. mesh	100 per cent minus 4 mesh	6,000
Feldspar	7½ × 10 ft. cylindrical	1.05	Closed	85	−¾-in. mesh	90 per cent minus 325 mesh	

applied to the cylinder in order to obtain a product having the desired combination of sizes.

Another type of screen is the shaking screen operated by a weight (Fig. 36). Often several layers of screens of various sizes can be superimposed in order to classify a product into a number of different sizes. Closed-in screens (Fig. 37) are used with dusty materials. For screening materials below 60 mesh, it has been found desirable to use air separators rather than screens, and very satisfactory classification devices can now be obtained to produce material down to 200 mesh or even finer.

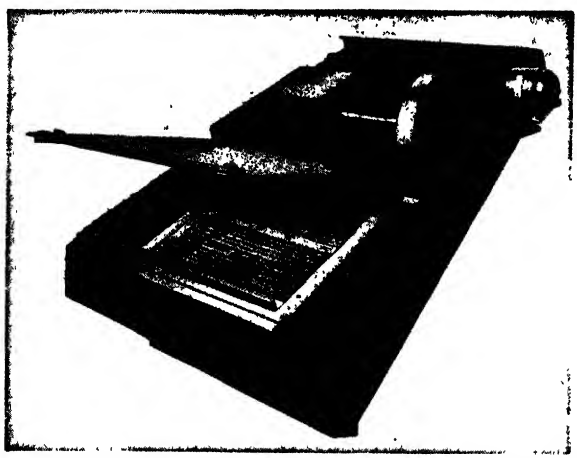


FIG. 37. A closed-type screen. (*Courtesy of the Deister Concentrator Company.*)

5. Mineral-dressing Methods. Many refractory raw materials can be purified by simple mineral-dressing methods. As the demand for refractories becomes more exacting and our supplies of the better raw materials less plentiful, concentration methods will be increasingly used.

Tabling. Minerals of a different specific gravity from the unwanted material with which they are mixed can often be efficiently separated by an air or water table. The raw material is ground fine enough to unlock the individual grains and then passed over an inclined vibrating table, which will give a more or less clean separation. Although this method has been used in the past mainly for the treatment of ore minerals, it has been quite successful in the concentration of kyanite from our North Carolina deposits.

Settling. Door-type thickeners and centrifuges[33] are used to remove coarse particles from clay slips as well as to dewater these slips.

Magnetic Separation. Powerful magnetic separators are now available that will remove all minerals containing even small amounts of iron.

These include the iron oxides, sulfides, and more complex minerals such as garnet, hornblende, and micas.

The magnetic method of purification is used quite generally with feldspars and other materials for whitewares, but it has not as yet been used extensively for refractory materials. However, there is opportunity of employing it with some refractories, such as those used in melting glass or enamel frits.

Flotation. Froth-flotation methods have been developing with such rapidity since 1920 that many separations can now be made that would have been thought impossible a generation ago. The method, in general, consists in stirring the finely crushed mineral in water with a frothing agent, which provides a multitude of fine bubbles. By selecting the proper agents, it is possible to get a selective action of the bubbles so that they adhere to certain types of particles and float them to the top of the water where they are carried off. Although considerable progress has been made with flotation methods in purification of minerals like feldspar, little has been done yet on refractory materials, but it would seem quite possible that this method would be well adapted to the concentration of chrome ores.

A little laboratory work has been done by flotation methods in removing iron minerals from fireclays, but as yet the results have not been shown to be economically feasible. Nevertheless, there is certainly promise that with further development along this line, second-grade clays can be so beneficiated that first-grade refractories can be made from them. Kellogg[28] describes a method of removing quartz from kaolin by flotation methods.

Electrostatic Separation. The electrostatic separator has been used to purify both feldspar and kyanite. The method consists in separating one type of mineral from another by virtue of the different attractive forces in a high-voltage field. This is a dry method and should not be particularly expensive except that the particles must be fairly fine before treatment. A patent by Weis[20] describes a method for removing quartz from kyanite.

Chemical Methods. Chemical methods can be used for the higher priced refractories. For example pure alumina refractories are produced from Al(OH) obtained from bauxite by the Bayer or other of the many processes[27] proposed for this purpose. Magnesium, with other chemicals, is being extracted from sea water[26] in considerable amounts and also is separated from dolomite. Beryllia is removed from the ore by chemical treatment[23,24,25] to give highly pure materials. The rarer materials such as zirconia, ceria, and the rare earths are all extracted by chemical means.

6. Storage of Clay. It is usually necessary to store a certain amount of clay to provide for interruptions in mining due to cold or rainy weather or holidays. The amount of needed storage depends on the length of

shutdown in the mining operation. To provide sufficient storage for a large clay plant is rather costly, and it is unusual to store more than a few days' supply.

In many of the ceramic industries, the practice is to weather, or age, the clay supply for a considerable length of time to develop plasticity and dis-

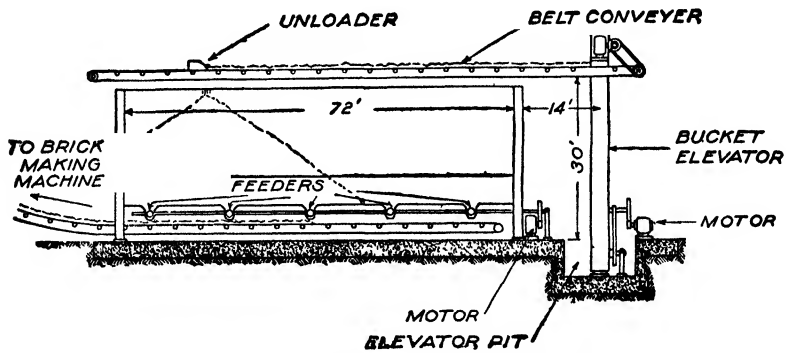


FIG. 38. A method of handling clay in storage bins.

integrate the lumps; but in the case of refractories, the amount of clay used is so large that this cannot be done economically, and only in the case of special high-grade clays can aging be resorted to.

Some of the high-grade refractory clays must be shipped a considerable distance by railroad. In these cases, it is desirable to dry the clay partially in order to reduce the shipping weight. This can be done by storing in

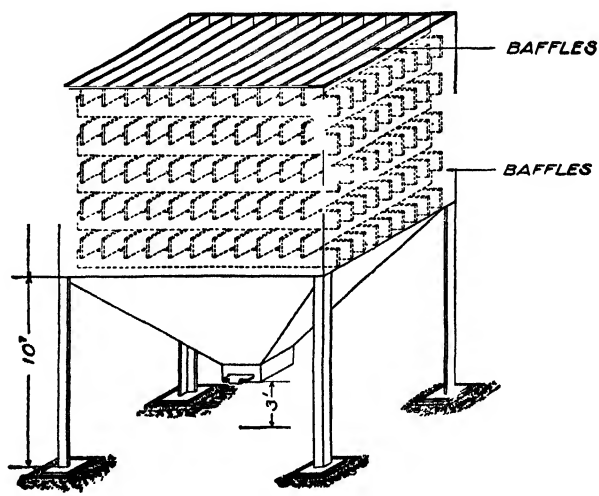


FIG. 39. Baffles for the prevention of segregation in bins.

open sheds or racks, where the moisture in good weather can be reduced to 5 or 10 per cent, or by passing it through a rotary drier.

Storage bins are made in various styles.[32] Some are cylindrical bins having conical bottoms; others are of a rectangular shape with a V bottom with provision for removing the clay from any portion desired (Fig. 38). The clay is usually put in the bin with a bucket elevator, but other handling methods such as grab buckets are occasionally used.

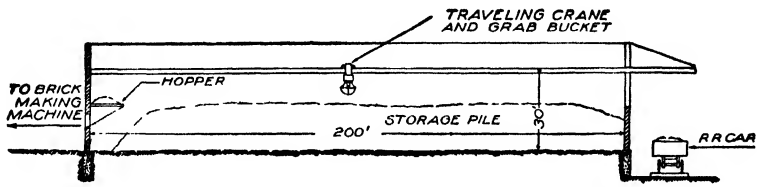


FIG. 40. An overhead crane and grab bucket for handling clay in storage.

When crushed materials such as clay or grog are to be stored, precautions must be taken to prevent segregation of the material in the bin. In nearly all manufacturing processes, it is highly desirable to have the crushed materials of a proper and uniform screen analysis. When the material from the crusher falls into the bin, the larger particles roll to the outside and the finer ones build up into a central cone. The material drawn from the bottom of the bin will contain at first mostly fine and later

FIG. 41. A modern storage system. (*Courtesy of A. P. Green Fire Brick Company.*)

CHAPTER VI

MOLDING METHODS

1. Workability of Clay. *Types of Flow.* Before entering into the discussion of workability of clays, it will be well to review a few definitions as adopted by the Society of Rheology.[38]

Fluid: A substance that undergoes continuous deformation when subjected to any system of finite shearing stress.

Solid: A substance that undergoes permanent deformation or rupture only when subjected to a system of shearing stresses that exceed a certain minimum value.

Simple (Newtonian) Liquid: A liquid in which the rate of shear is proportional to the shearing stress (for laminar flow).

Elastico-plastic Solid (the Clay-water System): A solid that obeys the law of an elastic solid for values of the shearing stress below the critical stress corresponding to the elastic limit in shear and that deforms plastically when the shearing stress exceeds that value.

Viscosity: In a simple liquid, the constant ratio of shearing stress to rate of shear.

Plasticity: That property of a body by virtue of which it retains a fraction of its deformation after the deforming stress is zero.

Elasticity: That property of a body by virtue of which it recovers its original size and shape after deformation.

Thixotropy: That property of a body which causes a decrease in shearing stress with time at a constant rate of shear.

Rheopecsy: That property of a body which permits agitation to accelerate the setting up of a gel.

Dilatency: That property of a body which causes an increase in shearing stress with time at a constant rate of shear.

The following symbols are generally used in flow problems:

F_0 = the yield stress in shear, dynes/sq cm

F = the shearing stress, dynes/sq cm

dv/dr = the rate of shear strain, cm/sec/cm

η_s = the coefficient of apparent viscosity of a suspension (dynes, sec, cm^{-2}) ($ML^{-1}T^{-2}$) (Poise)

η_1 = the coefficient of viscosity of suspending medium

η = the basic viscosity of suspension (at infinite rate of sheer strain)

C = the volume concentration of solid in relation to total volume

V = the volume flow, cc/sec

v = the velocity of flow, cm/sec

T = the time

In considering the clay-water system it is usual to separate it into two parts: the slips of low clay content and the plastic masses of high clay content. This is done because the sticky region between is incapable of accurate measurement at present and also because this region is not used industrially, but a more fundamental reason is that different laws seem to apply to the two cases. The slips will be considered first.

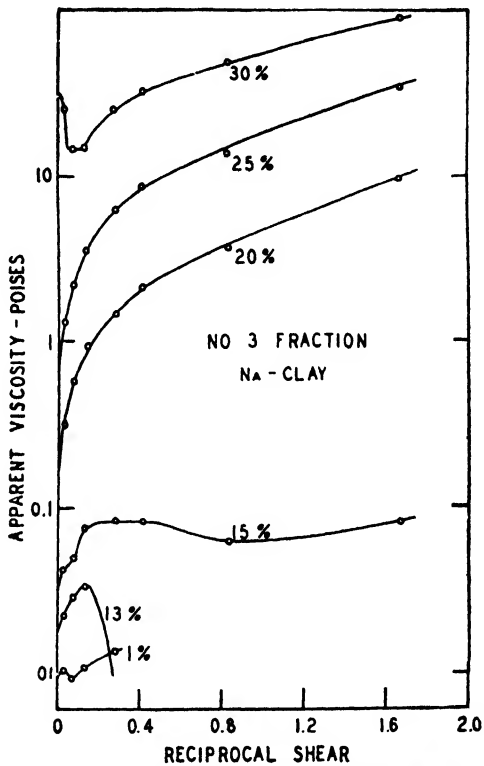


FIG. 42. Apparent viscosity of slips at different rates of shear. (*J. Am. Ceram. Soc.*)

Clay Slips. A simple liquid like water obeys the following relation in the viscous flow region:[49]

$$\eta = k\frac{F}{v}$$

The quantity η can be measured in many ways, but the revolving cup viscosimeter, as shown in Fig. 49, is very satisfactory for ceramic work. Here the viscosity is determined by the twist of calibrated wires, and thus a wide range of values can be covered. The rate of shear can also be varied over a wide range for the measurement of thixotropy in suspensions.

The viscosity of a suspension of spherical particles seems to show no change in apparent viscosity with varying rate of shear strain, but more work needs to be done to confirm this similarity to a liquid. Suspensions of anisotropic particles, such as clay particles, show a pronounced change in apparent viscosity with change in shear strain rate as shown in Fig. 42, and the coefficient of thixotropy θ is determined from the slope A/B of the curve at infinite shear rate.

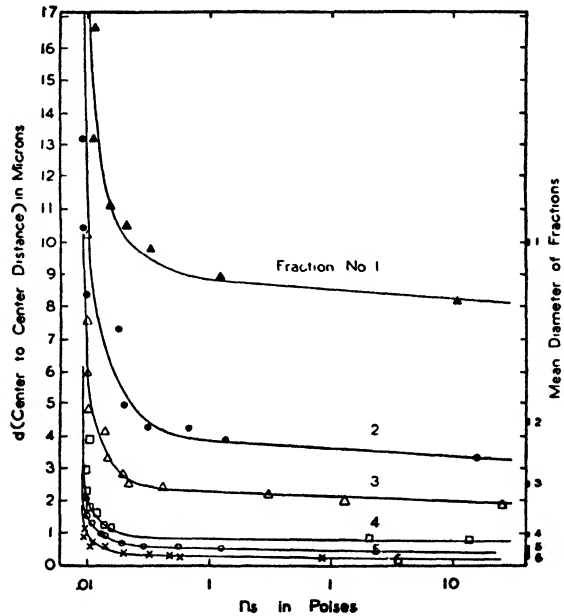


FIG. 43. Relation between viscosity and center-to-center distance of particles of six fractions containing Na kaolinite. (*J. Am. Ceram. Soc.*)

The apparent viscosity of a suspension is due to the sum of

1. The viscosity of the suspending medium
2. The energy absorbed by the individual particles revolving in the velocity gradient of the sheared fluid
3. The energy absorbed by the interference of the particles with each other

It is found that suspensions of monodisperse kaolinite[49] in either water or a dispersing electrolyte solution obey the following law:

$$\eta_s = (1-C)\eta_1 + k_1C + k_2C^3$$

where k_1 and k_2 are constants varying with the particle size and electrolyte in the suspending medium. The first and second terms predominate at low values of C, while the last term increases rapidly at higher concentra-

tions where the particles interfere. In Fig. 43 is shown the apparent viscosity of several deflocculated (Na-kaolinite) monodisperse suspensions on a basis of center-to-center distance of the particles, and it is clearly evident that as each fraction reaches a concentration such that the center to center distance is equal to the mean diameter of the particle, the viscosity increases rapidly. As a visual guide to the suspension, there are shown to scale in Figs. 44 and 45 two suspensions represented in Fig. 43.

The thixotropy of a suspension is given by

$$\theta = k_3C + k_4C^3$$

In the monodisperse kaolinite fractions, the value of θ is eighteen times the value of the corresponding viscosity. The units of viscosity divided

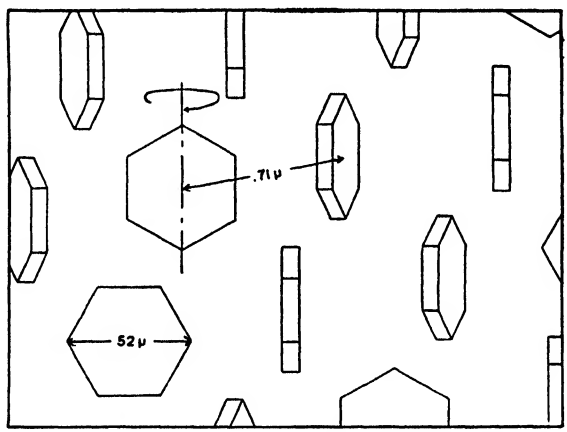


FIG. 44. Cross section of particles of No. 5 fraction containing Na Kaolinite at a viscosity of 0.017 poise and a volume concentration of 0.05 solid. (*J. Am. Ceram. Soc.*)

by the units of thixotropy give T^{-1}, or in this case $T = 0.05$ sec, which probably corresponds to the gelation interval. As yet no completely satisfactory explanation of the mechanism of thixotropy has been advanced, but it is probably due to a scaffold structure formed by the anisotropic particles.

The yield point of suspensions in water (H-kaolinite) may be shown to follow

$$F_0 = k_5C^3$$

over a wide range of concentration, k_5 varying with particle size. Well-deflocculated suspensions (Na-kaolinite), even in high concentration, show no measurable yield point.[49]

Figure 46 shows the influence of particle size and amount of ions added to a slip of constant solid content. The various-size fractions were

separated from a kaolin with a centrifuge and cleaned. Then definite amounts of sodium hydroxide were added in milliequivalents per 100 g of dry clay. The enormous and sudden reduction in apparent coefficient of viscosity on adding sodium hydroxide is evident in all cases. This is the principle of deflocculation, which permits fluid slips with low water content. The exact mechanism of deflocculation is not clearly understood at present, but it is believed that free OH ions over and above those absorbed on the clay are required to lower the particle charge and thus minimize the attraction forces between the particles, as discussed by Johnson and Norton.[78] These OH ions can be produced by the ionization of bases like NaOH or by the hydrolysis of salts like Na_2SiO_3. The positive ion accom-

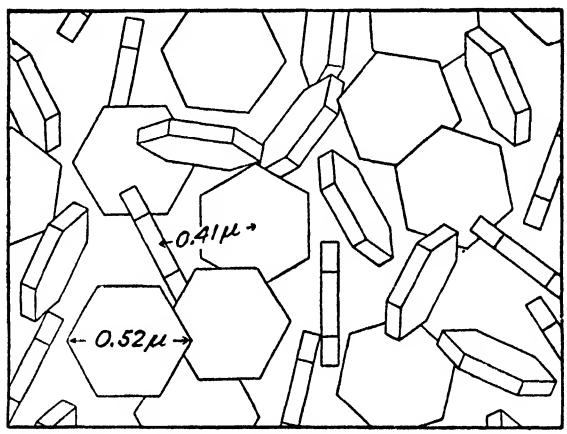


FIG. 45. Cross section of particles of No. 5 fraction containing Na kaolinite at a viscosity of 3 poises and a volume concentration of 0.28 solid. (*J. Am. Ceram. Soc.*)

panying the OH ion must be monovalent; therefore calcium or magnesium salts will not deflocculate. Some of the recent work in colloidal chemistry[34] would indicate that the suspended particles are in equilibrium between a repulsion and attractive force and that this equilibrium is varied by added ions. Other factors such as organic matter[36] and particle shape[34] are undoubtedly important, but at present there is not enough information on which to base any conclusions.

Plastic Masses. Turning now to the plastic masses with a high enough yield point to resist gravity forces, it is well to consider some fundamental principles. In general, the three-component system, clay-water-air, may be expressed in the somewhat conventionalized volume diagram for a low molding pressure shown in Fig. 47. Such a diagram is made up by thoroughly mixing and kneading clay and water batches of successively increasing water content and molding each in a cylindrical

steel die at the given pressure. Provision is made for the escape of excess water. The wet and dry volume and the wet and dry weight will readily allow the volumes of air, water, and clay to be computed, provided the specific gravity of the clay is known.

As the amount of water is increased, the total volume of the mix, which originally consisted of clay and air, shows little change as the pores become filled. At the critical point, all the voids in the clay are filled with

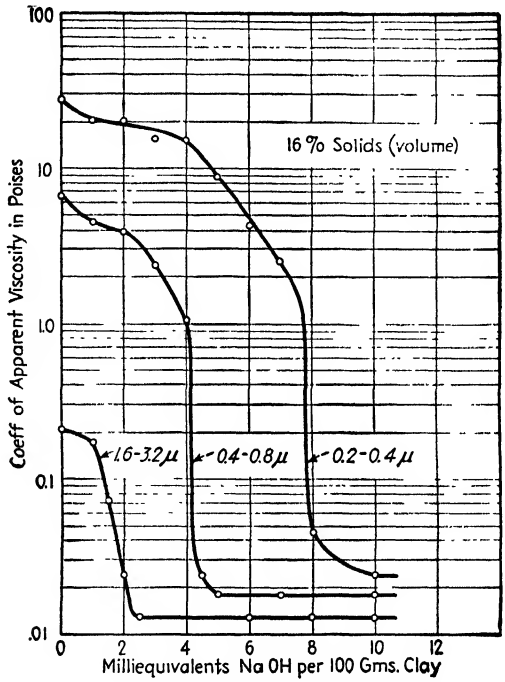


FIG. 46. Viscosity of kaolin slips.

water and the air phase vanishes. As the water is increased still further, the particles are separated by a film of increasing thickness until the maximum for stability is reached at that pressure. This may be termed the "saturation point." If more water than this was originally in the clay, it will be squeezed out in permeable pressing.

The critical point is a very important one, as above this point the mass shrinks on drying owing to the removal of the water films, as discussed in Chap. VII. The thicker and more numerous the films per unit length of clay specimen the greater the shrinkage. Below the critical point, there is little or no drying shrinkage. The critical point also is the dividing point between the consistency of a damp powder and a homogeneous plastic mass.

At a higher molding pressure such as would be obtained in a dry press, for example, the diagram would appear as shown in *a*, Fig. 47. Both the critical and saturation points are moved to low values of water content.

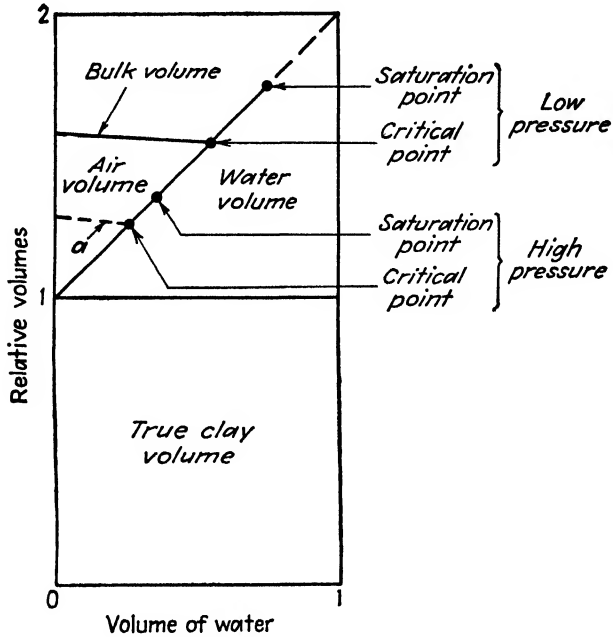


FIG. 47. The clay-water-air system.

There are often slight exceptions to the simplified diagrams shown here. For example, the total volume sometimes decreases slightly as water is added up to the critical point, for the water acts as a lubricant and allows closer packing. On the other hand, if the clay contains bentonite, the particles of which swell in water, drying shrinkage may occur below the critical point.

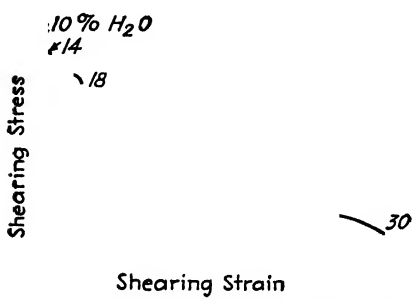


FIG. 48. Flow properties of a plastic body.

The flow characteristics of plastic masses are shown in Fig. 48 for various water contents.[30,40,48] The flow is elastico-plastic; and as the water increases, the yield point becomes lower while the maximum strain becomes greater.

Measurement of Workability. The consistency of slips is best measured in a concentric cylinder viscosimeter, such as that developed by Mac-

Michael. A modified instrument is shown in Fig. 49. In this instrument, an outer cup, which can be revolved on a vertical axis at various speeds, holds the slip. An inner cylinder is suspended coaxially with the outer cup on a torsion wire that measures the torque. By suitable calibration with standard sucrose solutions, the dial on the wire can be made to read the apparent viscosity coefficient of the slip in poises. In the case of slips, we have only to measure the apparent viscosity coefficient at various rates of shear to obtain all the desired rheological properties.

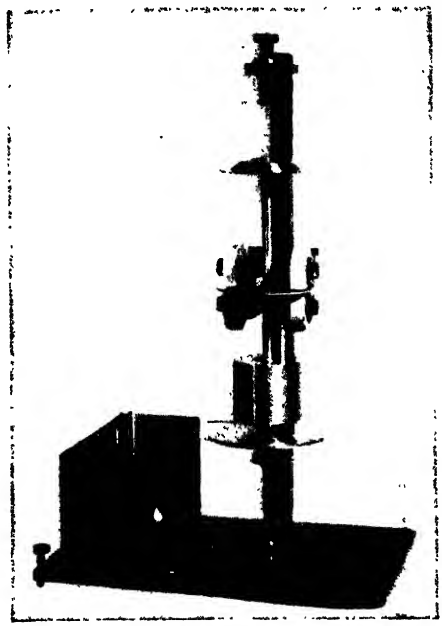


FIG. 49. Modified MacMichael-type viscosimeter.

In the case of plastic masses, not only the deforming force is required but also the maximum deformation at fracture. The most useful method for evaluating the workability factor is to twist a hollow cylinder and obtain the stress-strain diagram in pure shear. A satisfactory machine for accomplishing this, which was developed some time ago in the Ceramic Laboratory at the Massachusetts Institute of Technology,[40] is shown in Fig. 50.

The specimen *B*, with its brass end pieces, is clamped in the torsion head *C* by means of a wedge, as shown more clearly in the detailed sketch. This offers a simple and secure locking device, which prevents any backlash during the test. The torsion head is rotated by the motor *D* through the reduction gear *E*, the flexible couplings *F*, and the gears *G*. The motor

and reduction unit are mounted on spring suspensions H to prevent any vibration from being transmitted to the remainder of the apparatus. This drive gives a constant speed with sufficient power for any of the tests with plastic materials. The speed of the motor can be altered by the voltage

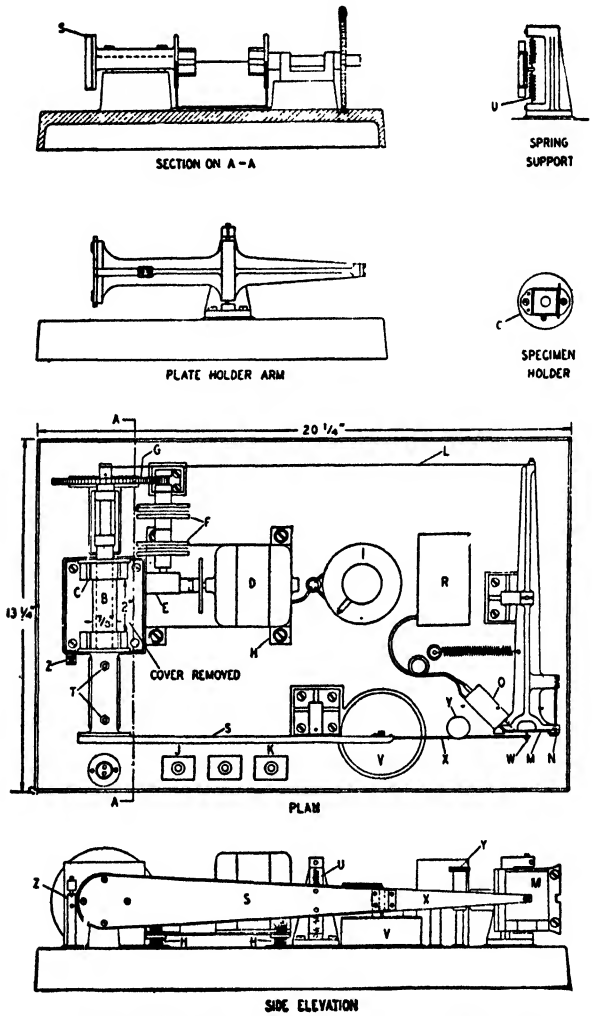


FIG. 50. Apparatus for measuring workability. (*Am. Ceram. Soc.*)

regulator I, and its direction is reversed by switches J and K, which independently control the separate field coils. In addition, the speed can be changed by various sets of gears at G.

The angle of rotation of the specimen is recorded by the steel tape L,

one end of which is wound around a drum on the torque shaft and the other attached to the plate-holder arm so that the angular rotation is proportional to the movement of the smoked plate *M*. This plate is held in a spring clip *N* and is illuminated from the back by the light *O* supplied by the 6-volt transformer *R*. This illumination is necessary for close observation of the stylus in relation to the zero line, as will be described later.

The torque on the specimen is measured by the deflection of the light aluminum arm *S*, which is pivoted on the center line of the specimen with the flexible steel emery knife edges *T*. The deflection of the end of the arm is, therefore, free from any friction effects and is proportional to the torque. In the case of the stiffer materials, the springs *U* are necessary to supplement the knife edges. Under these conditions, the vertical movement of the end of the arm *S* is proportional to the torque for the small angles employed. The movement of *S* is controlled by the dashpot *V*, filled with a light oil of a viscosity to give critical damping. Such damping is necessary when rapid movements of the arm occur in the initial portion of the stress-strain diagram.

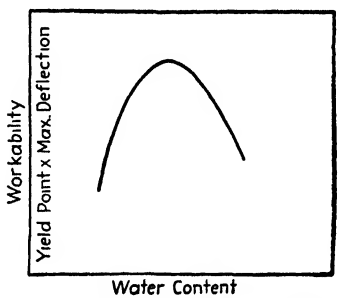


FIG. 51. Workability of a plastic body *vs.* water content.

The recording of the diagram takes place on the smoked glass plate *M* by means of a pointed steel stylus *W* held against the plate lightly by the thin steel spring *X* so that very little friction results. The stop *Y* allows the stylus to be removed from the smoked-glass plate after the completion of a record.

Referring back to Fig. 48, typical stress-strain diagrams of plastic clay at various water contents will be seen. The points to be noted are the yield point *a*, the twist at the breaking point, and the maximum torque. No one figure will represent the workability, but a high yield point and high deformation will give the best value. Roughly, the product of the yield point and the maximum deformation may be taken as the workability. If this product is plotted against water content, it will show a maximum value at the consistency of best workability,[30,46] as shown in Fig. 51.

The stress-strain diagram is altered by changing the rate of shear[40] so it is well to perform the tests at a shear rate comparable with that encountered in a particular forming process. Clay masses are elastic up to the yield point only under rapid deformations.

Numerous other methods have been mentioned for measuring workability, such as the orifice flow of Stull and Johnson,[47] the tension test of Hyslop,[31] and the cylinder-compression method of Roller,[45] as well as the many impression methods similar to the Vicart needle.

Mechanism of Workability. A new theory explaining the workability of clay masses has recently been proposed by Norton,[55] which may be called the "stretched-membrane" theory. The yield point exhibited by the plastic mass is explained by the compressive force exerted on it by the surface layer of water on the outside of the mass. This layer, as represented in Fig. 52, may be thick in soft masses (*a*), in which case the surface curvature between the particles is of long radius and the surface tension forces due to capillarity are low. At the same time the particles are widely separated by water films as evidenced by the great drying shrinkage from this condition. On the other hand, if some of the water is removed from the mass (*b*), it becomes stiffer due to the surface film's becoming thinner

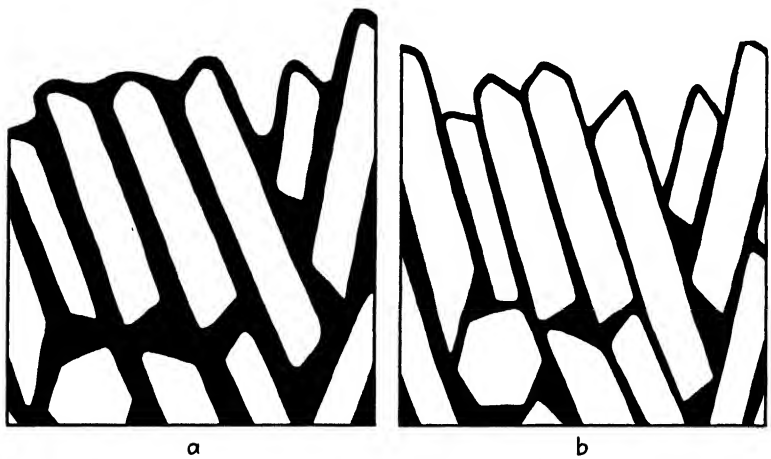


FIG. 52. Enlarged cross section of a plastic mass near the surface with varying amounts of water. (*J. Am. Ceram. Soc.*)

and drawing down into the capillaries with a smaller radius of curvature. This puts the mass of particles under higher compression and thereby forces them closer together. Now unless this compressive force is balanced by an interparticle repulsion force, the particles will come together until they touch. But we know they do not touch, because drying shrinkage occurs, indicating that the separation is something of the order of 100 molecular layers.

In Fig. 53 is shown the force field about a hydrogen clay particle as postulated by Hauser and Hirshon.[76] A flocked suspension settled out of water would be represented by point *B*, where the attractive and repulsion forces just balance. Under the forces of shearing the particles will be separated slightly, bringing attractive forces into play, which accounts for the yield point found in such a system. On the other hand, if a little water is removed from the system by compressing between porous pistons

(filtering) or by drying, the particles will come closer together, such as at point C, so that interparticle repulsion forces are built up just to compensate for the external compression produced either by the pistons or by the surface capillarity. Therefore, it is incorrect to say, as usually stated in colloidal literature, that the particles in a flocked system are held together by attraction forces; rather there is always an equilibrium between the external forces and the interparticle forces, the former compression and the latter repulsion.

It is rather difficult to visualize the forces acting in the clay mass as produced by the stretched membrane; however, the simple mechanical diagrams shown in Fig. 54 should make the picture clearer. In diagram *a* there is shown a series of spheres held apart by compression springs loosely fitting inside of a tube. The spheres represent the clay particles, the springs the repulsion forces, and the water surrounding them, the water in the clay mass. If two tightly fitting pistons close the ends of the tube and P_1 forces them together, it will readily be seen that the forces between the particles are not affected, and therefore, because of the incompressibility of the liquid, force P_1 is resisted entirely by hydrostatic compression forces in the water itself, thus allowing no appreciable contraction of the total volume.

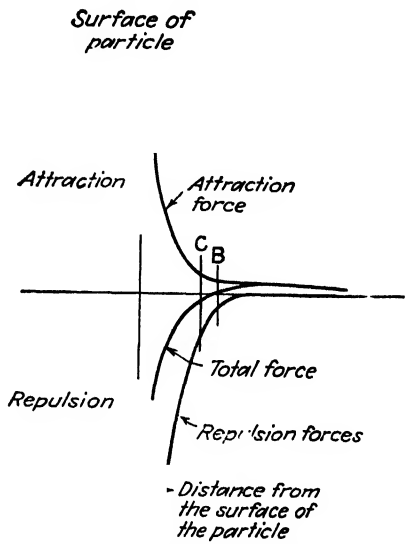


FIG. 53. The field of force about a clay particle when surrounded by water.

Suppose, however, that we substitute porous pistons as shown in diagram *b*, which represents the case of permeable pressing. In this case, it will easily be seen that now the force P_2 is not resisted by the water, as this can readily flow through the pistons. The force is consequently taken by the springs between the spheres; and if the pressure is large enough, these springs will be compressed until the spheres are actually touching.

Diagram *c* represents the condition occurring in the free plastic mass. Here tight pistons are used; and instead of the force P_1, a capillary force P_3 acts to put the water in hydrostatic tension. This action on the pistons will draw the particles together, compressing the springs, and gives closer packing *only in so far as water is removed by the capillary.*

Therefore, it can be seen that in the case of the plastic clay mass the capillary forces of the stretched membrane act to draw the particles closer

together and that this force is balanced by the repulsion forces between the particles.

The high capillary forces in wet clay are clearly brought out in the article by Westman,[20] where layers of clay were exposed to water on one side and nitrogen pressure on the other to balance the capillary forces. In this way, it was unnecessary to have a large column of water in tension,

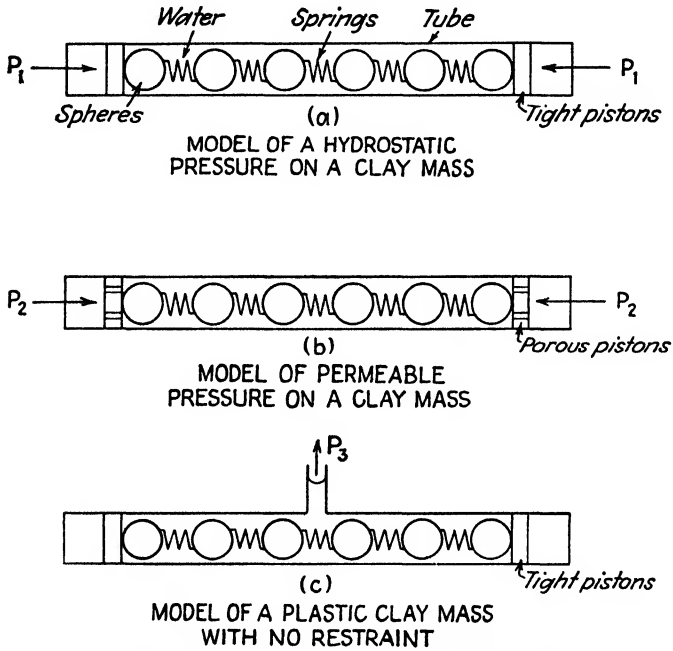


FIG. 54. Mechanical model of the clay-water system.

which was a limiting factor in some of the older tests of this type. Westman found, as we should expect, rather low capillary forces in the coarser grained flint or feldspar but higher ones in kaolin and very high forces in fine-grained ball clay. His values in pounds per square inch are shown in Table 21:

TABLE 21

Material	Pounds per Square Inch
Flint	5
Feldspar	10
Kaolin	263
Ball clay	880

This theory will account for the increasing yield point with decreasing water content, as well as for the greater workability in finer grained masses where the capillary forces are higher.

A very simple direct proof of this theory is to fill a thin rubber balloon with dry, powdered clay. The material then will act like a dry powder; but if the balloon is slowly evacuated, so that the atmosphere, pressing on the rubber, forces the clay particles together like the water film, then the mass assumes the identical plastic properties of wet clay.

Of course, the particles making up the mass have an important influence on workability. They should have a small size to produce small capillaries at the surface for a high yield point and numerous water films for good extensibility. Of all the natural materials, clay minerals have the smallest dimensions, a plate thickness of less than 0.1 μ. Then again an active surface to stabilize the water film is necessary, and here again the clay minerals seem to be unique in possessing large negative charges. The work of Wilson[30] gives some indication of how workability is connected with the size, shape, and composition of the particle, but more work of this nature is needed.

2. The Casting Process. *Casting Slips and Deflocculents.* The casting slip is a mixture of clays, nonplastics, and deflocculents proportioned to give the proper physical properties. A good slip should have in so far as possible the following properties:

1. A low enough viscosity to flow into the mold readily
2. A high enough specific gravity to prevent settling of the nonplastic
3. Ability to drain cleanly (in drain casting)
4. Capable of giving sound casts (in solid casting)
5. Stability of properties with aging
6. Quick release from the mold after casting
7. Rapid casting properties
8. Low drying shrinkage after casting
9. High dry strength after casting
10. High extensibility in the partly dried condition
11. Freedom from entrapped air

Considerable experience is needed to make up a good casting slip, as the selection and proportioning of the clays are of great importance. However, the deflocculation, which was formerly an art, can now be approached systematically. For example, samples of the dried or nearly dry ingredients can be mixed with water to make several series of slips, of different specific gravity, and to each series can be added various amounts of deflocculent. Viscosity measurements are now made on each sample, and the results plotted as shown in Fig. 55. The double minimum is probably due, as suggested by Dr. Hall, to the fact that the ball clay reaches a

minimum viscosity at a different pH from the kaolin. Point *A* might be selected as the conditions for a solid casting slip, and Point *B* for a drain casting.

It is well known that NaOH, as used to deflocculate pure clay fractions, will not work so well with natural clays containing soluble salts, such as calcium and various adsorbed ions. On the other hand, Na_2CO_3 or

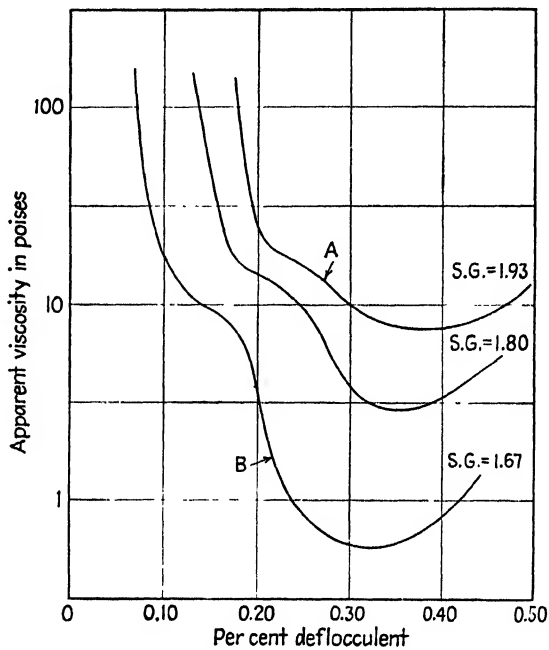


FIG. 55. Viscosity curves for clay casting slips.

Na_2SiO_3 do work well. The reason for this is that the latter deflocculents produce insoluble products while the former does not. For example:[77]

$$(\text{Clay-OH})_2\,\text{Ca} + \text{CaSO}_4 + \text{Na}_2\text{SiO}_3 \rightarrow 2\,(\text{clay-OH-Na}) + \textit{CaSiO}_3 + \text{Na}_2\text{SO}_4$$

or

$$(\text{Clay-OH})_2\,\text{Ca} + \text{CaSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow 2\,(\text{clay-OH-Na}) + \textit{CaCO}_3 + \text{Na}_2\text{SO}_3$$

The elimination of the troublesome Ca^{++} ions is thus accomplished. If necessary the SO_3^{--} can be taken out by adding a barium salt.

The mechanism of casting has been studied in considerable detail.[78] It consists essentially in the removal of the water from the slip next to the

plaster mold surface by capillary suction, and this removal continues deeper into the slip with increased time. However, as the water must pass through the layer of solidified slip, the rate of casting decreases with time. Fine-grained clays such as ball clays form a low permeability layer and are thus slow casting. Besides the water removal from the slip, there is also a flocculating action caused by the Ca^{++} and SO_3^{--} ions migrating from the mold surface into the slip, thus stiffening the cast layer.

In casting, there is some selective concentration of the finer materials on the mold surface and especially a preferred orientation of the clay plates parallel to the surface. This is readily proved by noting that a flat plate cast on one surface warps badly in drying and that the drying shrinkage parallel to the mold surface is less than normal to it.

There are many special deflocculents suggested in the literature, though not extensively used in practice. For example, sodium tannate,[66] salts of sulfonic acid,[75] humic acid, and many others have been used.

The casting of high-grog bodies such as glass pots, are well described by Heindl, Massengale, and Cossette.[79] They emphasize the careful sizing of the grog to give close packing and the selection of the clays to give the best casting properties. A typical slip composition is given in Table 22.[79]

TABLE 22. GROG CASTING SLIP FOR GLASS POTS

Material	Per cent
North Carolina kaolin	13
Georgia kaolin	9
Tennessee No. 5 ball clay	10
Kentucky No. 4 ball clay	10
Maine feldspar	5
Grog: 10–20 mesh	18
20–40 mesh	16
40–100 mesh	10
Through 40 mesh	9
Silicate of soda ("S" brand)	0 025
Sodium carbonate	0 012

There have recently been considerable developments in the art of casting nonplastics; and under the proper control, slips can be made up having casting properties equal to clay slips for either drain or solid casting. To illustrate, fused alumina is ground in a steel mill until the particles average 2 to 5 μ. The slip is acid treated and washed to remove the iron and then deflocculated with acid to give a pH of about 3 and a specific gravity of 3.0. In Fig. 56 are shown viscosity curves of a series of these slips to show the minima similar to those for clay slips. Properly made slips are nonsettling, shrink enough to release from the mold, and have fair dry strength

but must, of course, be handled more carefully than clay bodies. More details of this casting process are given in Chap. XII.

Molds. Space is not available here to go into the question of mold-making to any extent, but a few of the essential facts may be stated. Practically all the ceramic casting is done in plaster of Paris molds made

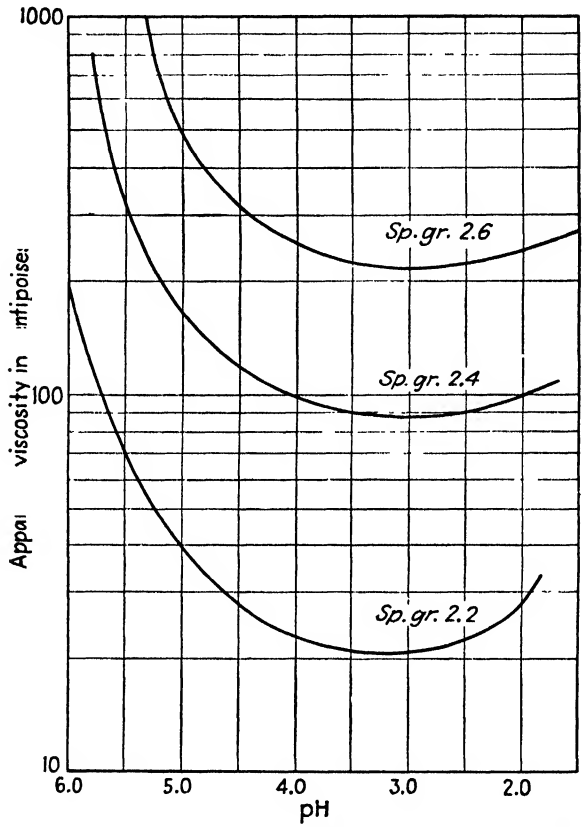


FIG. 56. Viscosity curves for fused alumina casting slips of 2 μ average particle size.

from a mixture of good pottery plaster and water. In a modern plant, the mixing is carried out with a high-speed mechanical mixer, as it is found that this method gives a more uniform mold and one freer from bubbles. A good average composition for a casting mold would be 36 lb of water and 40 lb of plaster, which is allowed to soak for 2 min and stirred for 3½ min, after which it is poured at once into the case or forms. Of course, the new batch of plaster must be prevented from sticking to the solid plaster case into which it is poured, and general practice in the ceramic industry is to

use a thick solution of soft soap (English Crown soap) and water to coat the surface of the solid plaster against which new plaster is to be poured. Apparently the soap forms an insoluble calcium compound on the surface of the plaster, which gives a polished surface with good wear resistance; consequently it is possible to cast a great many hundred molds from one case without losing accuracy.

The molds are made for two types of casting: The first is called a "drain casting," and the second a "solid casting." In the first type, the slip is poured into the dry mold until it is completely full and allowed to stand for a sufficient length of time to build up on the dry plaster a layer of body of the required thickness, as shown in Fig. 57. This may take anywhere from five minutes to an hour or more, depending on the type of piece. As soon as the required wall is built up, the liquid slip in the center is drained out, leaving a uniform casting. The top edge of the mold has to be designed in such a way that a true upper edge can be obtained readily on the finished piece. As shown in Fig. 57, a spare is generally used, so the level of the slip is somewhat above the top edge. After draining, the body is trimmed with a vertically held knife tangent to the plaster surface, which should project out just to the thickness of the cast wall. In this way, a true edge can be quickly obtained.

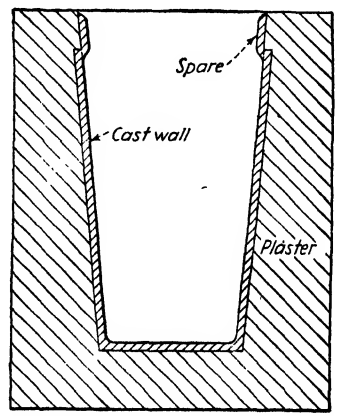


FIG. 57. Section of mold after draining.

When the slips contain large particles of grog, it would be obviously impractical to make drain castings, because the inner surface would be extremely rough. In this case, it is usual to make a solid casting in a mold, somewhat as shown in Fig. 58, for casting saggers. Here the slip is poured into the center of the mold and fills the annular space, rising up into the vent holes. A head of slip must be kept on the mold at all times because the solid casting gradually shrinks as the slip becomes solid and additional material has to be supplied to take up this shrinkage. In other words, the design for a mold for a solid casting is identical in principle with the design of molds for casting metal, where the gate has to be of sufficient volume to supply metal while the piece is solidifying.

Plaster molds naturally are comparatively soft and will wear after long use. It is a little difficult to give any exact figures on the life of a plaster mold, as this will depend on many factors. A mold for casting a fine-grained slip by the drain method may be made to give a hundred casts quite

satisfactorily if no fine detail is involved. Of course, the molds for casting grog bodies must take more wear and tear, but here we can afford to have considerable wear before the mold is discarded. The alkali used as a deflocculent in the slip will cause some deterioration of the mold, due to the salts being drawn into the mold where they become concentrated. It has been found that some of the organic deflocculents give a considerably greater mold life than the sodium carbonate and sodium silicate usually employed.

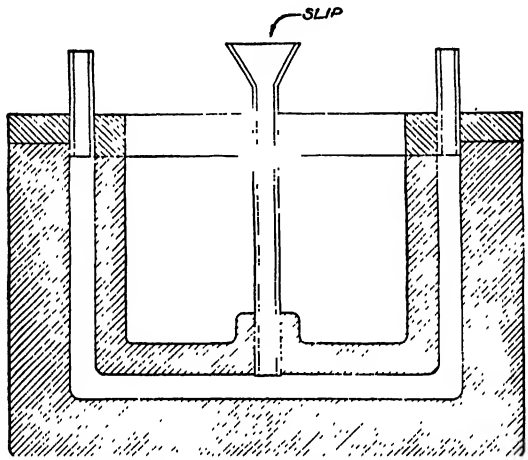


FIG. 58. A mold for solid casting.

Methods of Casting. The casting slip is made up by blunging the solid ingredients with water and a deflocculent. The slip is usually agitated for a considerable length of time in order to be sure that the clay is thoroughly wet and that the air bubbles are well removed. In some cases, the blunging is done with a high-speed mixer; in other plants, it is carried out in large vats with a slow-speed paddle. The fine-grained bodies for drain casting are generally made up in two stages; *i.e.*, the material is blunged up first with water to a rather thin consistency, passed through a screen of around 80 to 120 mesh and over a magnetic separator, and then filter-pressed to remove most of the water. The filter cakes are then reblunged with deflocculent[58,62,66] and some of the screened slip to make up the final slip. These steps are taken in order to make a sufficiently fluid slip to screen before the deflocculent is added. In the case of coarse-grained bodies, the slip is usually made up directly with the deflocculent.

The slip is often handled by pipe lines so that it can be fed under pressure to each casting bench, allowing the workman to fill his molds rapidly. In the case of the heavier slips, this cannot be readily done and the material

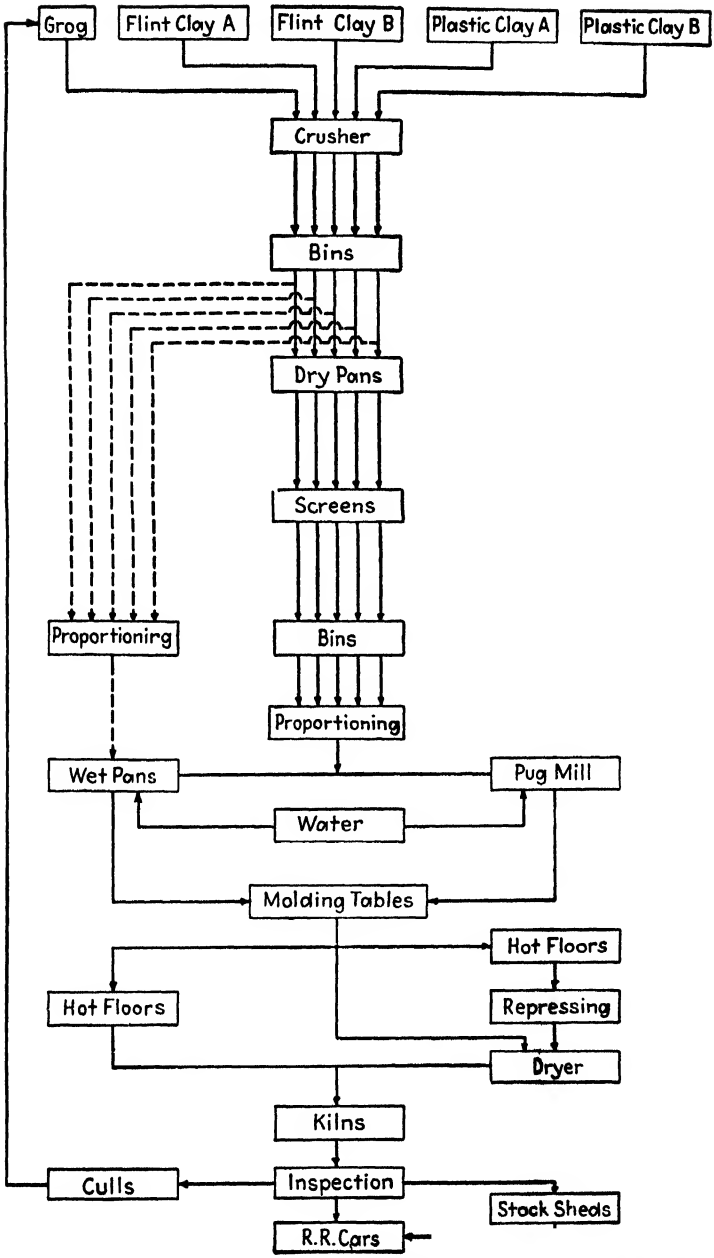


FIG. 59. Flow diagram for the manufacture of handmade brick. (*Courtesy of S. M. Phelps, American Refractories Institute.*)

is handled in hoppers. Sometimes it has been found desirable to deair the slip in a vacuum before casting in order to make a more dense structure. Some manufacturers prefer to use their slip at an elevated temperature, perhaps 90°F.

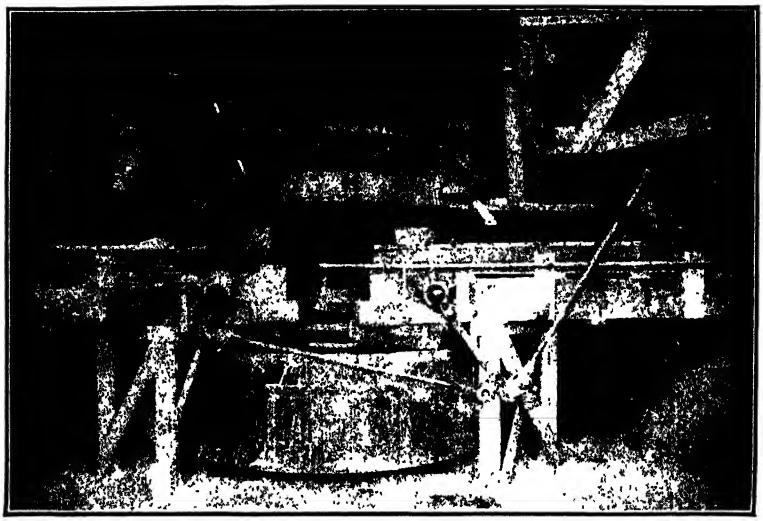


FIG. 60. A wet pan for crushing or mixing. (*Courtesy of Clearfield Machine Company.*)

The handling of the scrap trimmed from the cast pieces presents quite a problem, as it must be mixed back with the original batch in such a way as not to disturb the deflocculation.

3. The Soft-mud Process. The soft-mud process for making bricks, one of the oldest of all molding processes, has been used for making all types

FIG. 61. A pug mill for preparing clay. (*Courtesy of E. M. Freese and Company.*)

of brick from the earliest times. Although machines are available for making soft-mud bricks, they are used very little in the refractories industry, being confined to the manufacture of building brick; consequently here we will discuss only the hand-mold process.

The hand-mold method is used for making brick in both small and medium shapes. This process is particularly suitable for making certain types of special shapes, particularly intricate ones where the mold cost would be prohibitive by other processes. However, the total shrinkage is high, running from 6 to 12 per cent. Figure 59 shows a flow sheet of a typical hand-mold process. The individual clays are taken from the storage piles and crushed in a jaw crusher or dry pan, after which they are placed in overhead bins so that they can be removed by gravity. In one

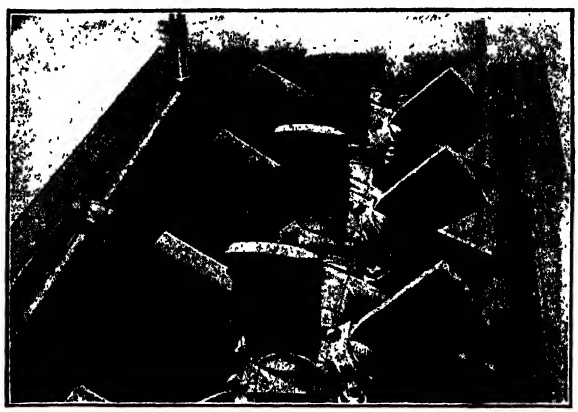
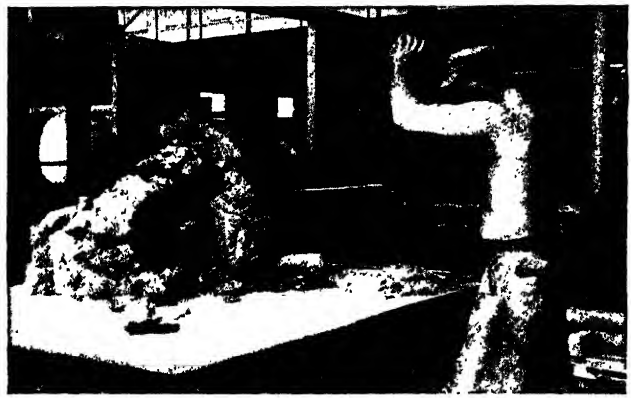


FIG. 62. Interior of a pug mill. (*Courtesy of E. M. Freese and Company.*)

process, the clays are proportioned in a batch and then fed to a wet pan (Fig. 60), where the whole mass is ground to the proper degree with water. Another method separates the grog into more or less definite-size fractions, which are then mixed together dry and the water mixed in either with a wet pan or with a pug mill (Figs. 61 and 62). The proper amount of water must be added to give a mix of the right consistency. A change of as little as 1 per cent can usually be detected by the molders.

The plastic mix is taken from the mixing machine to the molders' table located near the hot floor. The hand molder rolls a homogeneous slug of clay, sometimes called a "walk," of a little more than the volume of the mold. This slug is then lifted over the head and thrown with considerable force into the mold, where the inertia forces it into every corner. If more than a few pieces are to be made, the mold is usually made of hardwood lined with $\frac{1}{16}$-in. steel sheets. Sometimes loose pieces line the mold,

(*a*)



a. Building up the "walk."

(*b*)

b. Forming the sides.

(*c*)

c. Forming the ends.

FIG. 63. Method of

(d)

d. Throwing the "walk" into the mold.

(e)

e. The "walk" thrown on the mold.

(f)

f. Bumping.

hand molding shapes.

(g)

g. Cutting off the cap.

(h)

h. Slicking.

(i)

i. Placing on the hot floor.

FIG. 63 (*continued*). Method

(j)

j. Stripping mold.

(k)

k. Removing loose pieces.

(l)

l. Assembling mold.

of hand molding shapes.

which may be a single mold or may be divided by partitions to make a number of units.

The clay is prevented from sticking to the mold by dusting the wet mold with sand between moldings or oiling it with brush or spray. When the mold has been filled, it is violently bumped to consolidate the clay; then the excess portion is cut off with a wire, and the top slicked down. In the case of the larger shapes, it is necessary to fill the mold with several walks of clay, but care must be taken to avoid lamination. The mold is then dumped either on the hot floor or on a pallet, and the piece is allowed to dry.

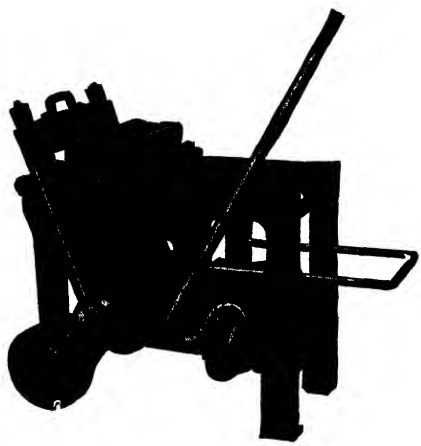


FIG. 64. A hand re-press. (*Courtesy of International Clay Machinery Company.*)

The fine series of photographs in Fig. 63 shows the steps in molding a shape by this process. Usually, hand-molded pieces in the standard sizes are hand re-pressed; *i.e.*, the hand-molded piece with a water content for stiff-mud consistency is placed in an oiled-steel die box (Fig. 64) and pressed to give an accurate shape and put on the brand.

Perhaps 3 per cent of all standard-shape fireclay refractories are now made by the soft-mud process, a percentage much lower than it was ten or fifteen years ago. In addition, a considerable proportion of the special shapes are made by the soft-mud process. A hand molder and a boy can mold approximately 400 standard bricks per hour, and a hand re-presser and two off-bearers can handle up to 550 bricks per hour, a rate that demands very skillful operation of the re-press. In hand molding special shapes from soft mud, a molder and helper will turn out about seventy-five 9-in. equivalents per hour.

It should be recalled that in the soft-mud process, the clay contains an amount of water somewhere between the critical point and the satura-

tion point, which allows the plastic mass to be deformed with a comparatively small force without rupture and yet permits it to have a sufficiently high yield value to prevent the shape from slumping after it is removed from the mold. However, the yield value is only slightly above the gravity forces, as any shock or jar on the freshly molded shape will make it deform.

The handmade brick are of open structure, quite resistant to spalling, and easily cut by the bricklayer.

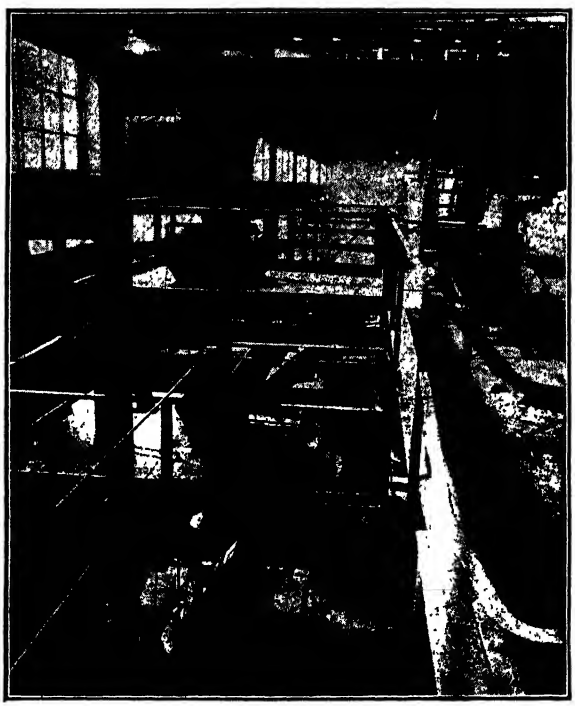


FIG. 65. A machine for molding silica bricks. The mud is dropped from the upper hopper into the mold below. (*Courtesy of Harbison-Walker Refractories Company.*)

Silica brick are usually made by the soft-mud process. The ganister is given a short treatment in a wet pan, when about 2 per cent milk of lime is added. The comparatively nonplastic mix is thrown into molds in the same way as for hand-molded clay bricks. However, the molds are steel, and push blocks have to be used in stripping because of the low strength of the brick. Since the yield point of the mix is very low, care must be taken not to jar the finished piece until it becomes dry.

Machines are now used for molding silica brick. The hydraulic press is used to some extent in this country and largely abroad, using about

4 per cent water and 5,000 psi pressure, but a dropping machine[81] that simulates hand molding has been quite successful in this country. It (Fig. 65) is entirely automatic, dropping slugs of the silica mix into the mold on a heavy anvil, slicking, and stripping. In this country lime alone is used as a bond, but in Europe sulfite liquor is used in addition.

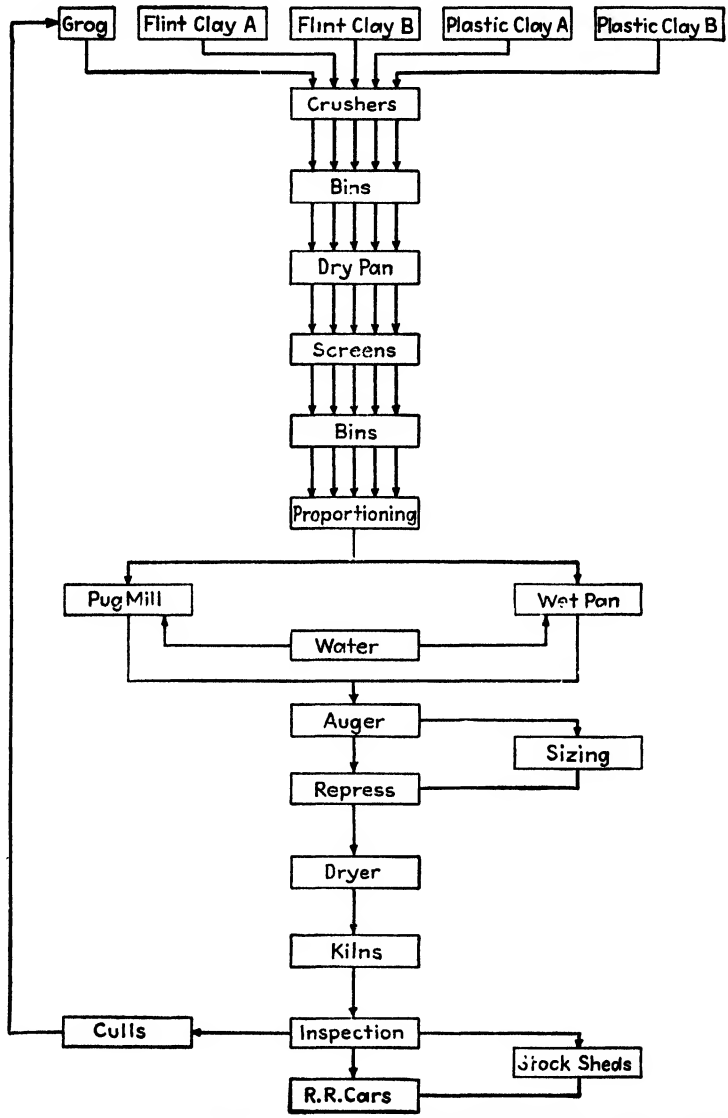


FIG. 66. A typical flow diagram for the manufacture of stiff-mud brick. (*Courtesy of E. H. Van Schoick, American Refractories Institute.*)

4. The Stiff-mud Process. The stiff-mud brick are made with a consistency just above the critical point; therefore considerable force is required to form the clay. Most of the refractories made by this process are formed by forcing the plastic material through a die from which it emerges as a more or less homogeneous column that can be cut off into definite lengths. This column is generally produced by an auger, consisting of a propeller-shaped screw running in a trough, which forces the clay with high pressure through a die. Steam-pressed brick are forced through a die with a piston operated by steam pressure, an intermittent process.

A flow sheet of the stiff-mud process is shown in Fig. 66, in which the clays are prepared in much the same way as for the handmade bricks.

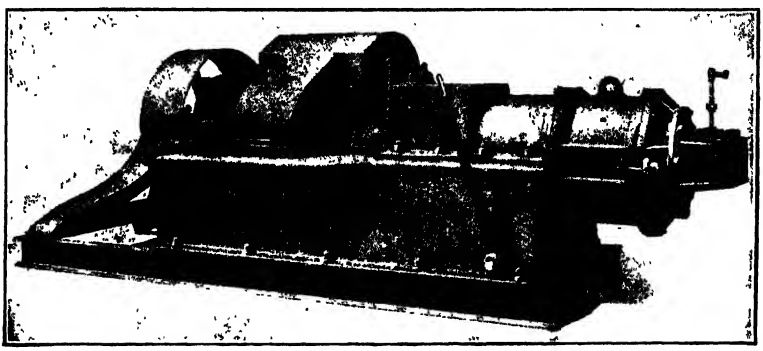


FIG. 67. An auger for producing a uniform column of clay. (*Courtesy of W. A. Riddell Company.*)

Water is added to the mixture with either a wet pan or a pug mill. The latter is generally preferred because it is a continuous process and better adapted to feeding the auger. The pug mill (Figs. 61 and 62) is a long, trough-shaped container with one or two horizontal shafts running down the center, having attached to them suitable blades for kneading and mixing the clay and propelling it gradually toward the exit end. Water can be added to the material in the pug mill to bring the mixture to the proper consistency.

The auger, as shown in Fig. 67, must be a well-designed machine in order to produce a uniform column. It is important in designing the die to assure an even velocity of the clay in all parts of the stream to prevent strains. Also the auger must be designed so as to prevent laminations, which often occur in the center of the column as an S-shape crack. The die itself is generally lubricated with oil to reduce the friction, and often it is steam heated for the same purpose. It has been found that if the clay is mixed in the auger in a vacuum chamber,[87,89,93] the air is readily removed and a more dense and homogeneous column is produced in

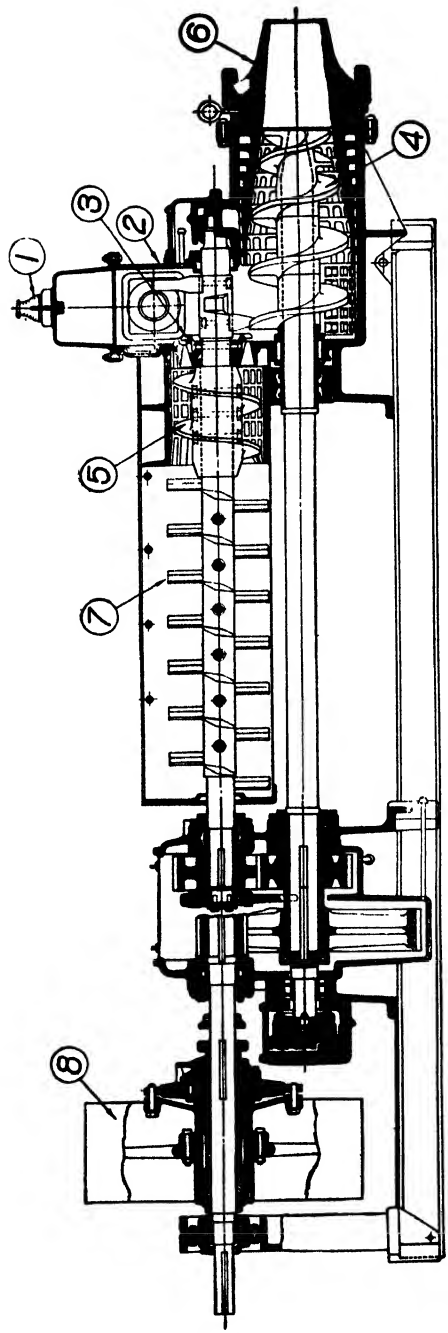


FIG. 68. Section of dearing auger. (*Courtesy of The Fate-Root-Heath Company.*)

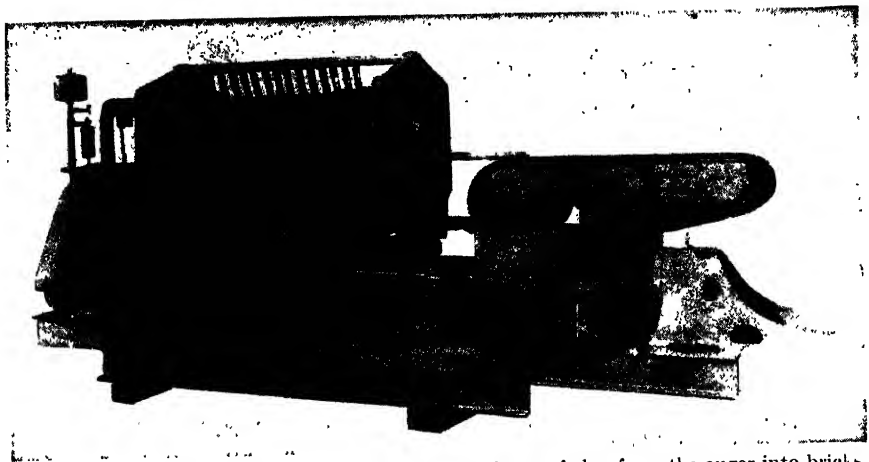


FIG. 69. A multiple-wire cutter for dividing the column of clay from the auger into bricks. (*Courtesy of The Bonnot Company.*)

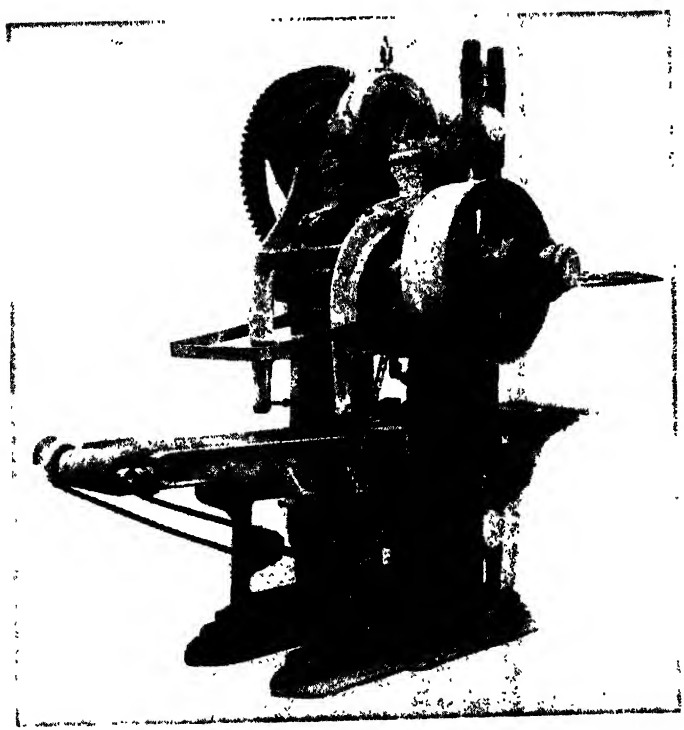


FIG. 70. A machine re-press. (*Courtesy of The Bonnot Company.*)

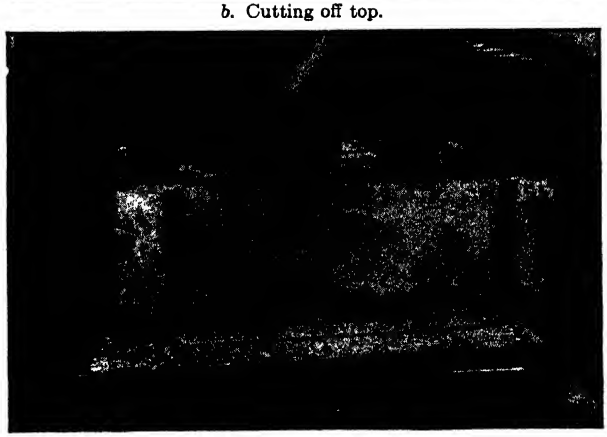
(*a*)

a. Ramming (note continuous feeding).

(*b*)

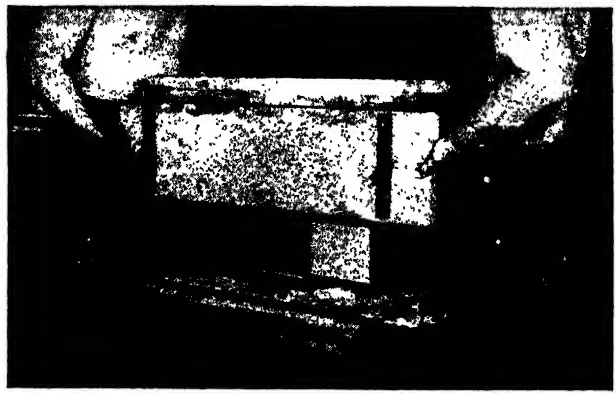
b. Cutting off top.

(*c*)



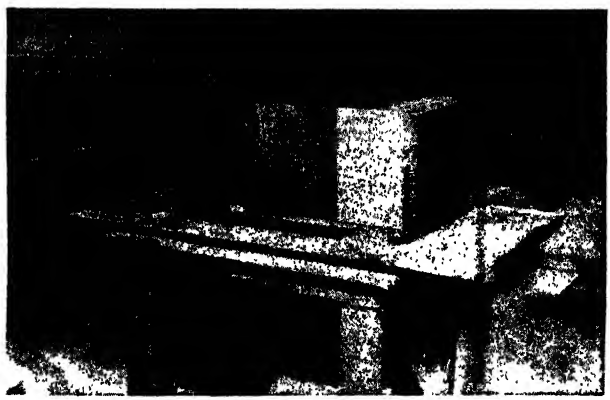
c. Slicking.

FIG. 71. Method of air



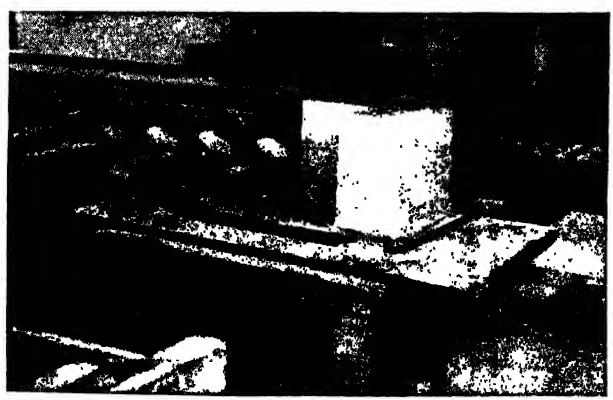
(*d*)

d. Stripping.



(*e*)

e. Showing loose pieces.



(*f*)

f. Finished block.

ramming of stiff-mud shapes.

passing through the die. One method of deairing in the auger is shown in Fig. 68. Deairing has now become a very common practice in stiff-mud operation and enables the production of sound bricks from clays that previously could not be readily handled. It also permits a denser structure to be obtained. However, deairing is not necessary for all bodies, as many of them can be handled quite satisfactorily without it. In fact, deairing seems to make some plastic mixes harder to dry and burn.

The column of clay from the auger is cut into uniform sections with a wire cutter, as shown in Fig. 69. Many designs of cutter are available, but they all operate on the principle of passing one or more steel wires through the column. It is difficult to operate a wire cutter satisfactorily if the grog content of the body is very high or if the size of the grog is very large.

There are few cases where the wire-cut brick produced are sufficiently uniform in size for use as refractories. Therefore the general practice is to pass them through a machine re-press as shown in Fig. 70, where they are actually formed to size and the brand put on. After being re-pressed, the brick are quite firm and can be readily handled and stacked on the drier cars.

Since stiff-mud brick have a strong tough structure, are good bricks for cutting, and are quite resistant to abrasion and slag, they can be used wherever a dense, strong brick is needed.

It is estimated that approximately 22 per cent of the fireclay refractories made in this country are produced by the auger and re-press. Inasmuch as an auger will produce as many as 6,000 bricks an hour and one machine re-press will turn out from 1,500 to 2,200 bricks per hour, four re-presses are generally set up with one auger.

Small, fine-grained refractories, such as tubes, can be extruded readily. If the plastic content is low, binders and lubricants can be added to give good flow properties.

A good many shapes, especially the medium and large ones, are made with a stiff-mud mix containing a high grog content because of the small total shrinkage and low warpage, even though the labor cost is higher than for the soft-mud method. Hard maple molds lined with $\frac{1}{16}$-in. steel are generally used, often with loose pieces. The mix is fed in slowly and continuously by one man while the other consolidates it with an air hammer having a corrugated foot. The whole process is clearly shown in the photographs of Fig. 71.

5. The Dry-press Process. In the dry-press process of making refractories, the clay has the consistency of a damp powder containing perhaps 7 to 10 per cent water. Only by high pressure can it be consolidated into a homogeneous mass. The flow sheet for the dry-press method is

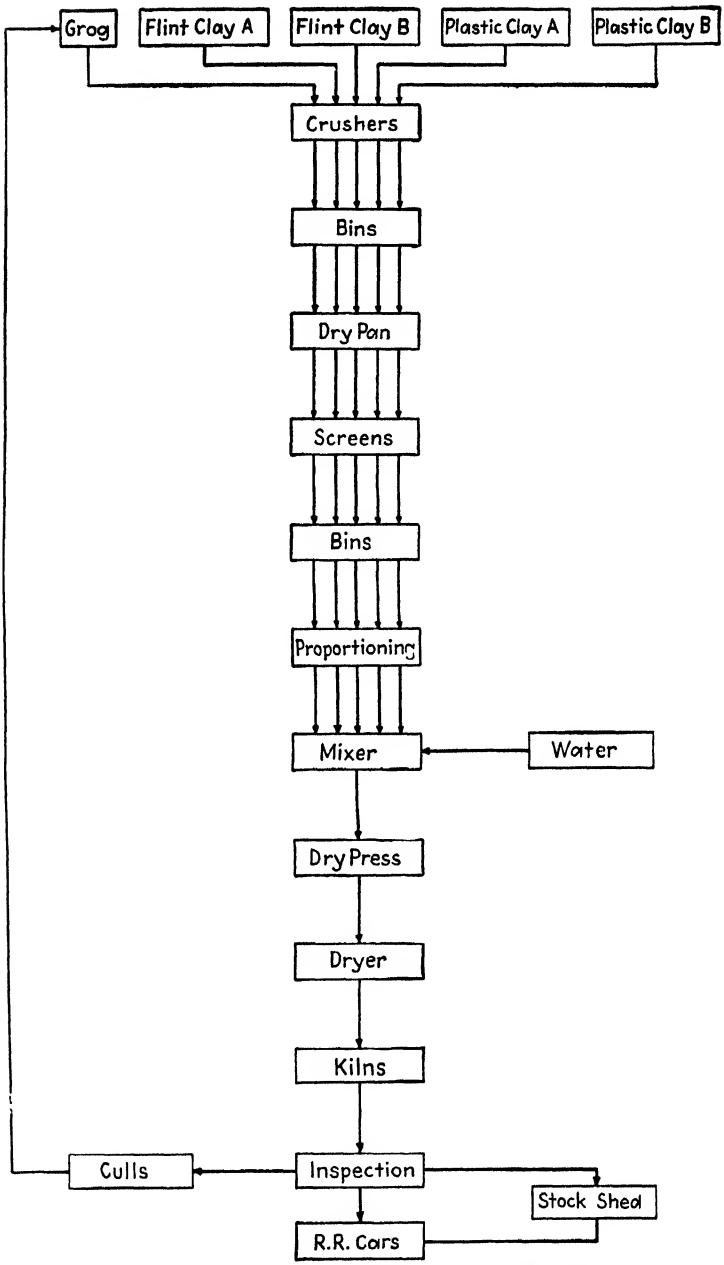


FIG. 72. Typical flow diagram for the manufacture of dry-press refractories. (*Courtesy of A. C. Hughes, American Refractories Institute.*)

shown in Fig. 72, in which the preparation of the clays is very much the same as for the preceding processes. In the Missouri district, the clays and grogs are often coarsely crushed, stored in bins, and recombined by feeders into dry pans, where they are further ground, screened, and tempered. The mix is aged for 24 hr and then fed to the presses. Modern practice seems to be favoring the more careful control of the sizing of the grog and flint clays by screening and recombining in definite proportions. The mixture of dry materials is then moistened in a pan or a pug mill and brought up to the proper consistency. Certain types of special

FIG. 73. A dry press in operation with the brick set directly on the tunnel kiln car. (*Courtesy of the Harbison-Walker Refractories Company.*)

mixers[95] are used to a considerable extent for this purpose. The mixed material is delivered to a hopper over the dry press, where the mixing action is continued, and permitted to flow into the dry press as needed.

The dry press itself (Fig. 73) is usually the toggle type, pressing four standard bricks at one time. However, hydraulic presses are used for certain types of refractory. The operation of the toggle press will be shown clearly by the excellent diagrams, prepared by Dr. G. E. Seil, in Fig. 74, which shows the various cycles in the pressing process. In order to make uniform brick, it is essential that the mix be uniform, that the same weight of the material be always charged into the dies each stroke, and that it be evenly distributed in the die box.[97,99] For nonplastic mixes like magnesite and chromite, a small amount, about ¼ of 1 per cent, of organic binder such as dextrine is used.

Until recently, the exact pressures in the toggle press were not known precisely. Now[96,97] they can be determined by the stretch of the side arms, which indicate pressures as high as 14,000 psi. With many materials, the maximum pressure is limited by the expansion, which causes pressure cracking, of the entrapped air on releasing the pressure. Recently, many presses[98] have been fitted with vacuum attachments that pull

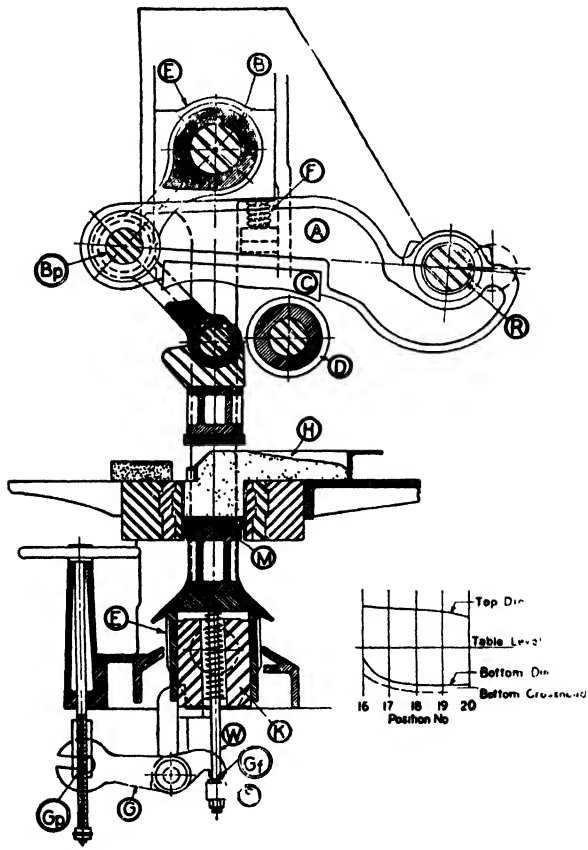


FIG. 74*a*. This figure shows the various cycles in the operation of a dry press when forming a brick. (*a*) Represents position No. 18. The crankshaft *R* has reached position No. 18 and has moved connecting beam *A* to its most forward position. The toggle pin *B* and connecting beam have now entered the portion of the cycle where they follow the radius of upper toggle *B* to position No. 2, where the lifting shoe *C* again comes in contact with lifting roller *D*. The side bars *E* have traveled from their topmost point at position No. 13, to their lowest point at No. 18, compressing equalizing spring *F* and bringing with them the upper toggle *B*, the lower crosshead *K*, and the pressure-adjusting mechanism. They pivot at point G_p, cause point G_f to press on saddle bar *S* and, by the tension placed on saddle rod *W*, they bring the lower die *M* to a level predetermined by the setting of point G_p. The charger *H* remains at rest until position No. 14, at No. 18 it has removed the finished brick and has begun to return to rest after it has filled the mold boxes. (*Prepared by Dr. G. E. Seil, E. J. Lavino and Company.*)

the air out of the die box and mix as soon as the top pad enters the box. Slots about 0.007 in. wide in the pads connect to the vacuum system.

The brick discharged from the dry press can usually be set on the tunnel kiln cars with little or no drying. The rate of forming dry-press brick on the toggle press runs between 1,000 and 2,000 brick per hr. The dry-press process is used very extensively in the industry, and it is

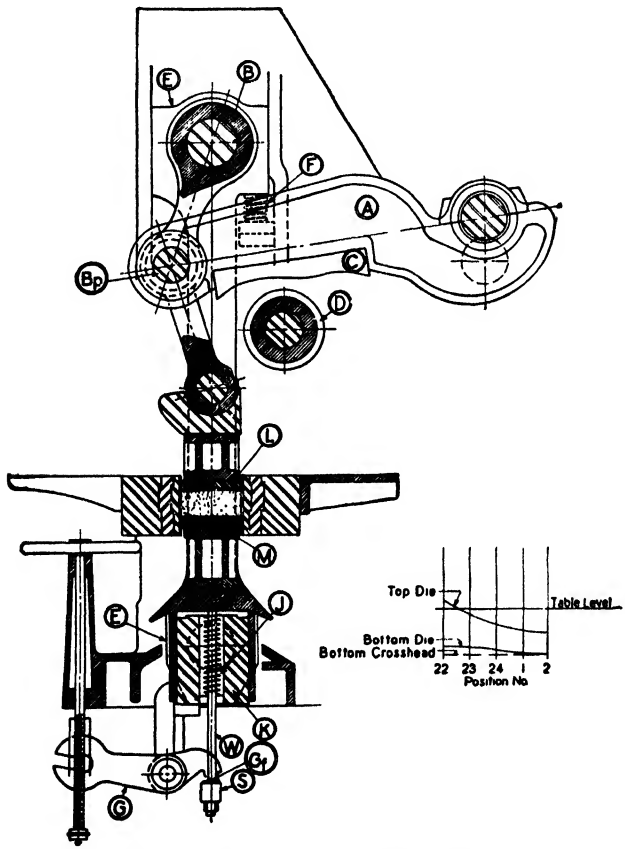


FIG. 74*b*. Represents position No. 24. At position No. 24 the connecting beam *A* and the upper toggle pin B_p are about midway along the arc made by the upper toggle *B*. The lifting shoe *C* has not yet come in contact with the lifting roller *D*. The side bars *E*, the upper toggle *B*, the lower crosshead *K*, and the pressure-adjusting mechanism *G* remain in the same position as No. 18. The upper die *L* has moved from its peak position at No. 16 to No. 24, where it has come in contact with the loose material and has slightly compressed it. The lower die *M*, which had been stationary from No. 18 to No. 23, has now moved to a new level owing to the pressure of the upper die on the now partly pressed material. This action compresses saddle springs *J*, lowers saddle rod *W*, and saddle bar *S* from point G_f on the pressure-adjusting mechanism. The equalizing spring *F* remains as before. The charger *H* has returned to rest at No. 20.

estimated that 70 per cent of the fireclay refractories and practically all the magnesite and chrome refractories are made by the dry-press process.

The bricks produced by dry pressing are very uniform in size, with strong corners and edges and little tendency to warp. They have good spalling resistance and generally good resistance to load.

The thickness of the dry-pressed piece is limited by the side-wall friction to about 4 in. in the conventional press, but numerous attempts have been made to improve this condition. In one method developed in Germany,[176] the bottom platen is vibrated while pressure is applied to

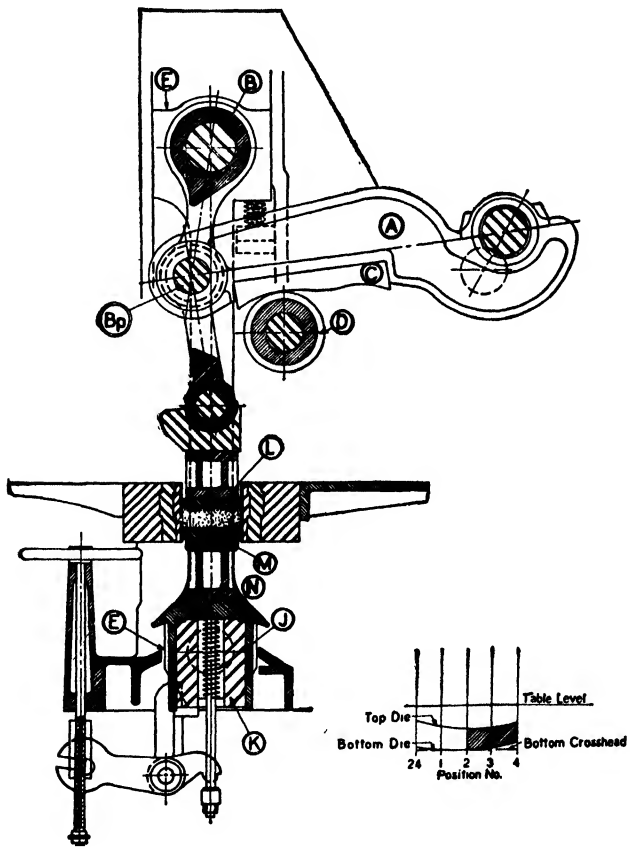


FIG. 74c. Represents position No. 2. At position No. 2 the upper toggle pin B_p and connecting beam A have completed the movement along the radius of upper toggle B, and have now brought the lifting shoe C in contact with lifting roller D. The side bars E remain in the same position as shown in Figs. No. *a* and No. *b*. The upper die L has further compressed the material, but has not yet pressed the brick to its finished size. The pressure of the top die on the material has caused the lower die M to compress fully the saddle springs J to where the saddle plate N comes in contact with the lower crosshead K.

the top one. In another, the sides of the mold box are oscillated up and down, so pressure is maintained between the platens in an effort to minimize the wall friction. Much work has been done by the powder metallurgist in studying the pressure distribution in pressed powders by

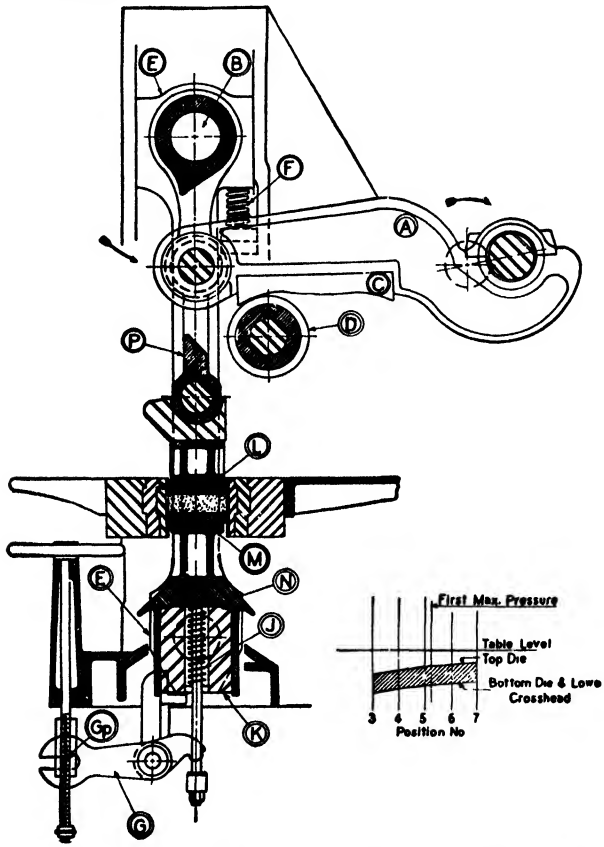


FIG. 74*d*. Represents position No. 5-¼. At position No. 5-¼ the first maximum pressure is reached and the material is pressed to its finished thickness. The side bars *E*, the upper toggle *B*, the lower toggle *P*, the upper die *L*, and lower die *M*, and lower crosshead *K* have continued to rise owing to the action of the connecting beam *A* and lifting shoe *C* on lifting roller *D*. At this point the side bars have lost contact with equalizing spring *F*, saddle plate *N* is still in contact with lower crosshead *K*, while saddle springs *J* are still fully compressed. The pressure-adjusting mechanism *G* has been rising with the lower crosshead using point G_p as a pivot.

incorporating a lead grid into the mass and later studying its deformation by X-ray pictures.[177] Here it was found that the proper wall lubrication did much to equalize the pressure.

When molding small dry-pressed pieces, it is common practice to use a lubricant or plasticizer to permit a more even distribution of pressure

and to minimize die wear. Some of the lubricants used are waxes, both water soluble and emulsions; stearates; fatty oils; polyvinyl alcohol;[114] and cetyl alcohol. Inorganic binders can also be used to increase plasticity and green strength. Commonly used binders are gelatin, dextrin, flour, starch, gums, and cellulose. In addition, an antisticking agent is sometimes added, such as a sulfonic acid, to aid removal from the die. The

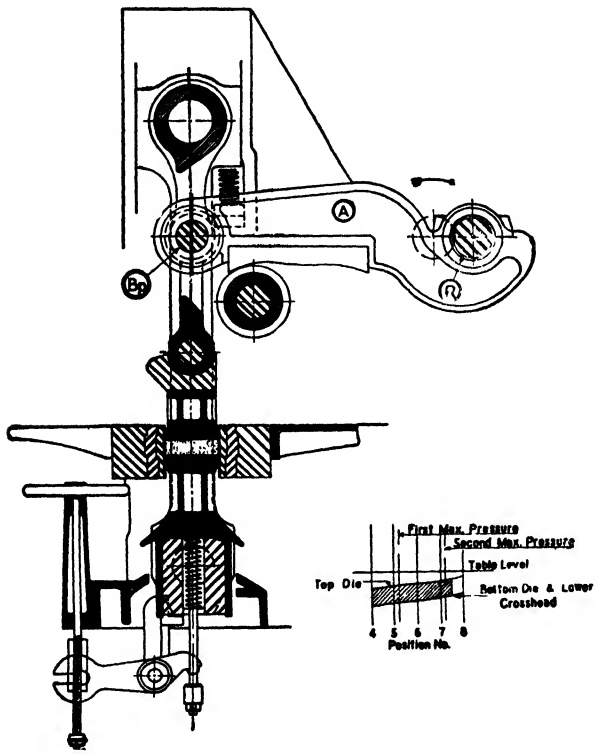


FIG. 74*e*. Represents position No. 6. Conditions at position No. 6 are changed slightly. The side bars have risen a little higher and the crankshaft R has reached its maximum throw, bringing connecting beam A to its extreme horizontal movement and toggle pin B_p over the center line of the side bars.

total amount of additions to the mix will generally run from 0.1 to 10 per cent. A good description of these organic additions is discussed in the references.[113,110,111,108]

The molding of carbon blocks is carried out with a heated mix of coke and tar pressed into molds for the smaller pieces and rammed with an air hammer for the larger pieces.[176]

Mixes of the dry-press consistency can be molded by hand ramming under special conditions. A patented process known as the Scheidhauer

and Giessing process uses a deflocculated slip of clays[176] mulled into carefully sized grog. The resultant mix contains about 90 per cent grog and 10 per cent clay, with a total water content of 5 to 6 per cent. By heavy ramming in rigid steel molds, large shapes can be made with a total shrinkage of not more than ¼ of 1 per cent. The photographs in Fig. 75 show clearly how a large tile is made by this process. A modifica-

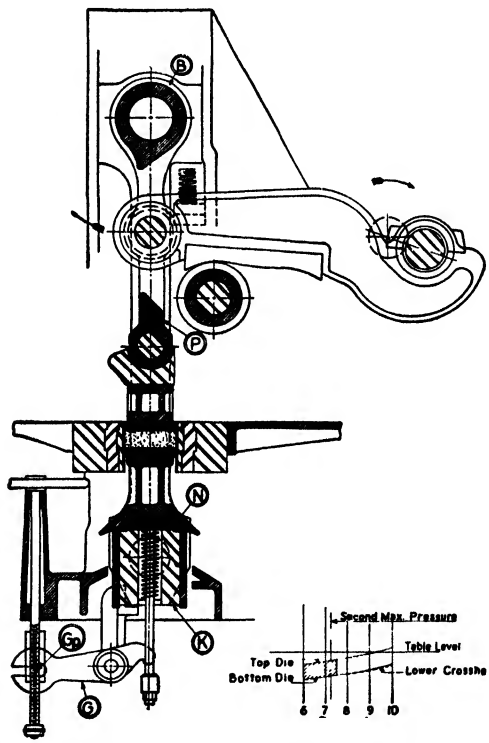


FIG. 74*f*. Represents position No. 7-¼. At position No. 7-¼ maximum pressure is again developed as upper toggle *B* and lower toggle *P* again pass over the center line of the side bars. The saddle plate *N* is still on contact with the lower crosshead *K*, where it will remain until No. 8 is reached. The pressure-adjusting mechanism *G* is still rising with the side bars *E* and lower crosshead, using G_p as a pivot.

tion of this method is described in a patent to Singer and Beken,[112] where the coating slip is flocculated before pressing.

6. Hydrostatic Molding of Refractory Powders. Hydrostatic pressing methods have been used quite successfully in the compaction of metal and refractory powders not particularly adaptable to slip casting or other methods of molding.

The powder to be pressed is graded by the usual methods in order to obtain the correct particle-size distribution offering the best packing

densities. As is shown in Fig. 76, a rubber mold is supported by an aluminum-segmented container, the latter mounted in the loading jig as shown. The steel mandrel, which defines the internal shape of the refractory body to be pressed, is located by means of a recess in the top

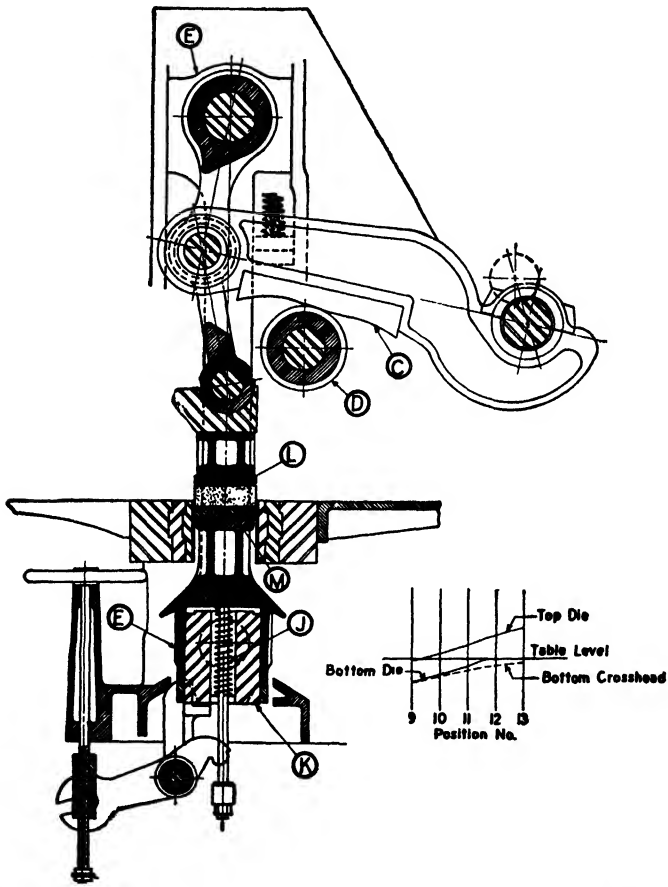


FIG. 74*g*. Represents position No. 11. At position No. 11 the side bars *E* have almost reached their highest point. The saddle springs *J* have come into action and have begun to push the lower die *M* to table level removing the finished brick. The upper die *L* has been rising slightly faster than the lower crosshead *K*. The brick is held against its face by the pressure of the saddle springs. The lifting shoe *C* is still in contact with the lifting roller *D*.

platen of the jig and held firmly by a stud bolt. The retainer ring, which supports the top of the aluminum segmented container, is also held in position by a recess in the top platen of the jig. The top platen assembly is held securely against the spacer rods by means of large wing nuts.

The dry powder is fed through slots in the top platen and vibrated to obtain good packing. A tamping tool, inserted through the powder-loading slots in the top platen, may also be used to ensure this condition. After the mold is loaded, the upper platen of the jig is dismantled (the steel mandrel is left in the mold) and the rubber retaining cup is slipped

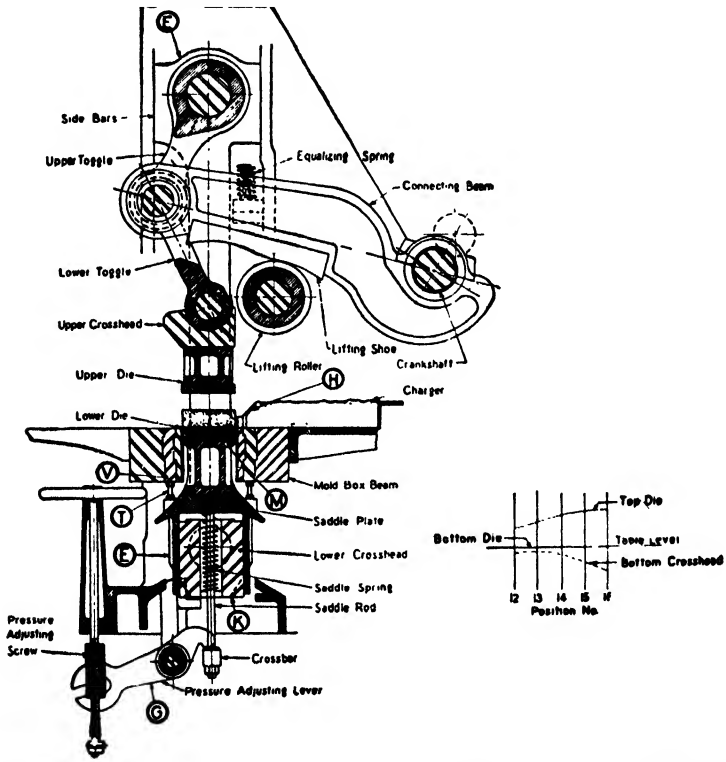


FIG. 74*h*. Represents position No. 14. The crosshead *K* at No. 14 has passed its highest point. The lower die *M* has been raised to table level where it is stopped by bolts *T* striking mold-box beams *V*. The charger *H* at this point has begun to remove the finished brick. The downward motion of the side bars *E* and crosshead *K* has lowered the pressure-adjusting mechanism *G*.

into place. The stud bolt is used to keep the rubber retaining cup in position, but the retaining ring and aluminum container are removed.

The rubber mold assembly consisting of the rubber wall form, the refractory powder, the rubber retaining cup, the steel mandrel, and stud bolt are now ready for loading into the hydrostatic chamber by a screw eye attached to the top of the stud bolt.

The hydrostatic chamber (Fig. 77) consists of a heavy steel-walled cylinder equipped with a self-sealing plunger, as suggested by Dr.

Bridgeman at Harvard, consisting of a two-piece plunger and a neoprene washer between three triangular-section brass rings. Water, with rust inhibitor added, is put in the chamber with the rubber mold assembly, and the plunger is inserted. As load is applied to the plunger by a hydraulic press, some of the air entrapped in the cavity is allowed to

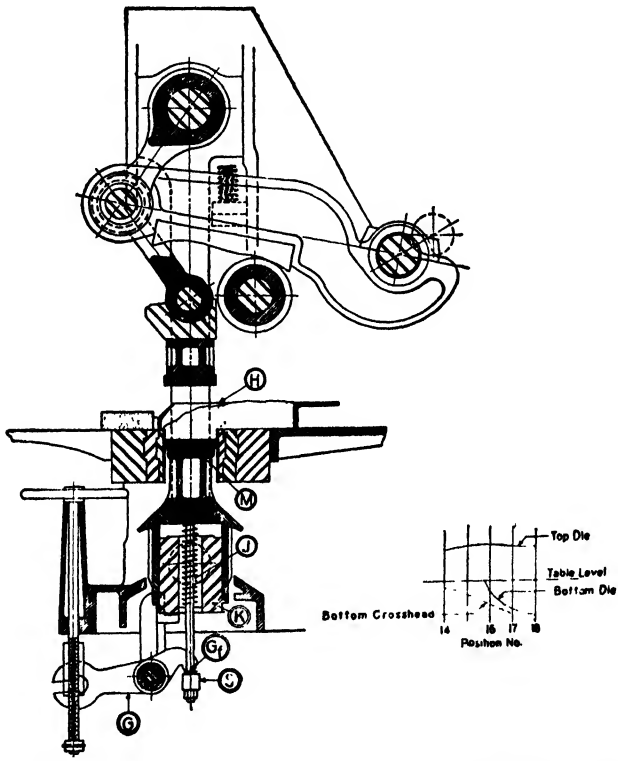


FIG. 74*i*. Represents position No. 16. At position No. 16 the crosshead *K* has continued to move downward taking with it the pressure-adjusting mechanism *G* until point G_1 comes in contact with saddle bar *S* and starts to compress saddle springs *J*. The setting of the pressure-adjusting mechanism decides the length of movement of the lower die *M* and allows the mold box to be filled to the desired depth. The charger *H* has further removed the finished brick and has started to fill the mold with loose material.

squeeze out between the plunger and the accurately honed bearing surface of the chamber. As more load is applied, the neoprene washer is deformed and is forced against the cylinder surface. At a very high pressure the brass rings tend to expand and, essentially, reinforce the neoprene seal. In general, pressures of 100,000 psi are used for the hydrostatic pressing operation. After pressing, the load is released, the plunger disassembled and removed, and the rubber mold assembly is lifted from the chamber,

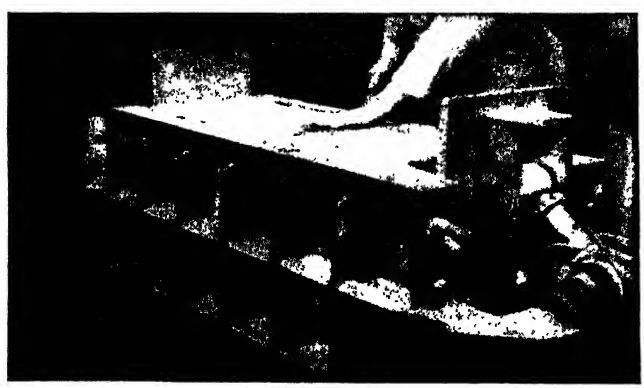
(*a*)

a. Air ramming.

(*b*)

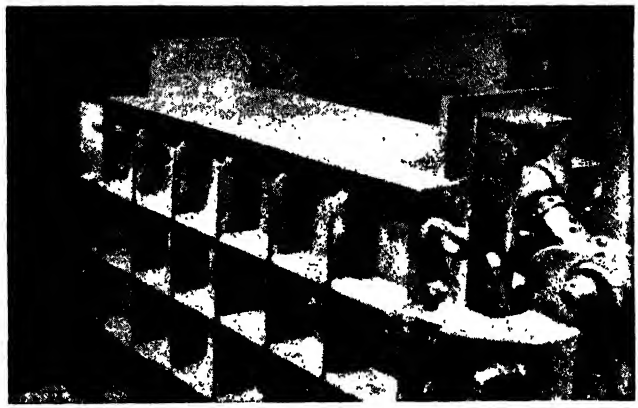
b. Cutting off the top.

(*c*)



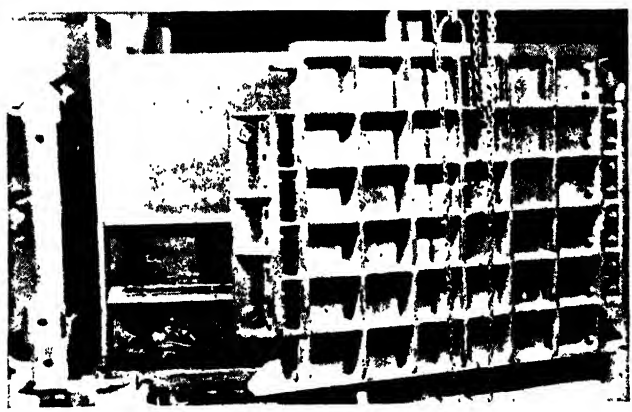
c. Finishing the top.

FIG. 75. Making a large tile



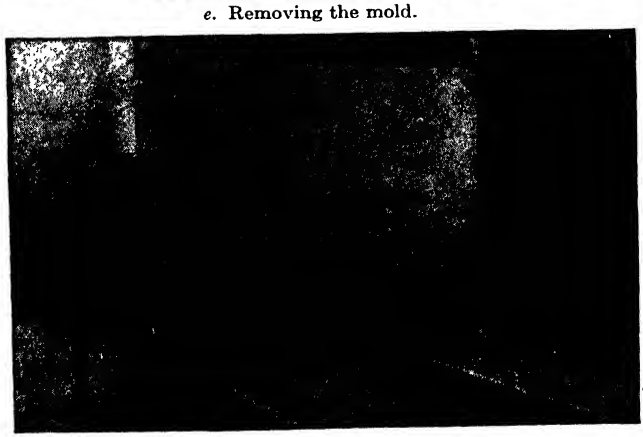
(*d*)

d. Finished block.



(*e*)

e. Removing the mold.



(*f*)

f. Block ready for drying.

with a low water-content mix.

dried, and, in turn, dismantled. If the surface of the mandrel is smooth, the refractory body can be removed easily and, surprisingly enough, is strong for handling even though no bond is used. On firing, the shrinkage is very uniform, so that any tendency to crack or distort is minimized.

7. Molding of Insulating Firebrick. The production of highly porous, lightweight refractories requires somewhat different methods from that employed for the heavier materials. Therefore, it was thought advisable to devote a special section to the molding of this product. An excellent review of this subject is given by Foster.[125]

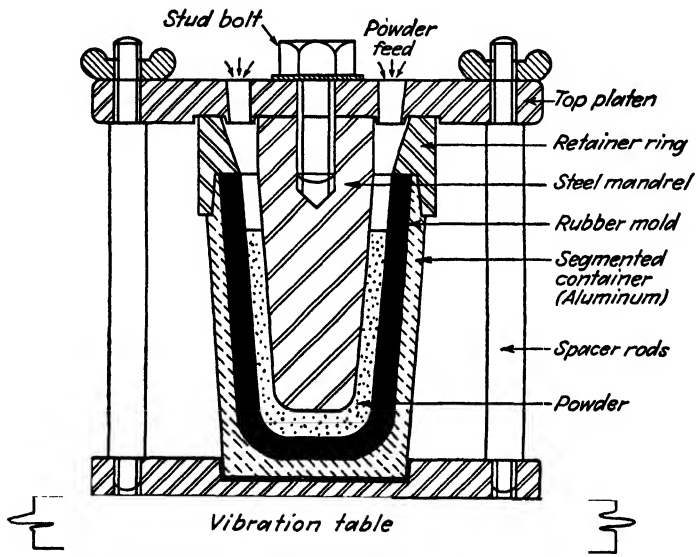


FIG. 76. Method of charging rubber molds.

Method of Obtaining Pores. Perhaps the most common method of producing pores in a fireclay product is to introduce in the plastic mix an organic material that later on can be burned out to leave voids. Sometimes this organic material may be peat, which is naturally mixed with the fireclay, but usually it is necessary to add granular organic material such as ground wood, cork, or other materials of this type. Of course, the properties of the finished product will depend not only on the clay but on the size, shape, and amount of the organic particles.

A somewhat different method of producing pores consists in adding to the clay mix granular sublimable material such as flake naphthalene.[121] When the ware is dried at high temperature, the naphthalene can be sublimed, leaving pores in the dried-clay product. The naphthalene vapor

can be cooled and used over again. Although this process has been employed industrially, it is not in common use at the present time.

Still another method of forming the pores in the clayware is to introduce into the clay, which has been made to the consistency of a thick slip, bubbles of gas that are sufficiently stable to remain in the mix until the

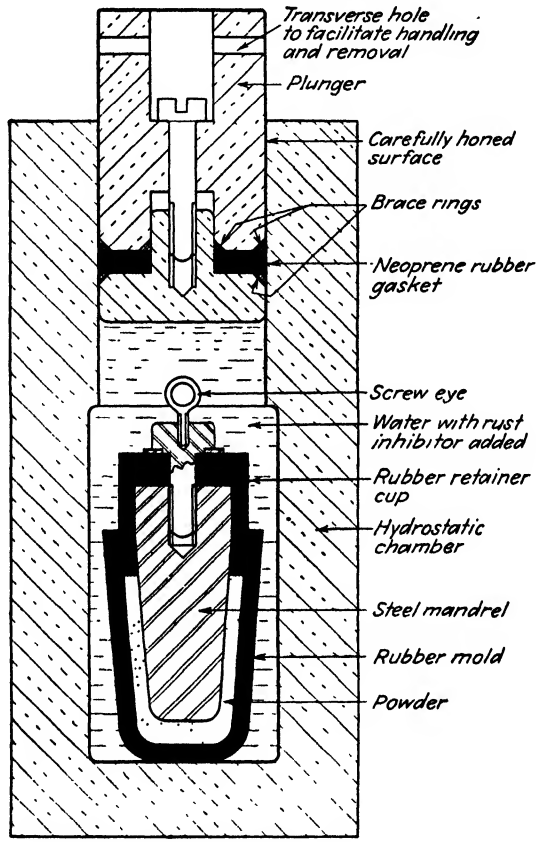


FIG. 77. Hydrostatic chamber for molding.

material is dried and burned. This method seems very attractive, as the cost of the organic material is eliminated; but practically, difficulties are encountered in stabilizing the bubbles so that they are of uniform fine size and evenly distributed throughout the mass. The method patented by Eriksson[120] produces bubbles in the clay mix by the addition of powdered aluminum or zinc and alkali so that each particle of aluminum is decomposed and forms a bubble of hydrogen. Others accomplish the same effect by stirring finely divided lime into the soft mix and then acidifying, with

the result that each particle of lime is decomposed, forming a bubble of carbon dioxide. Still another method, such as those patented by Ericson[119] and Roos,[124] consists in making a preformed foam, which is then stirred into the clay slip. Such a foam, of course, has to have considerable stability in order that this process may be successful.

All the bubble-structure refractories must have some stabilizing device to hold the bubbles as individuals and prevent their coalescing into larger ones. In the Husain and Bole[122] patents, this is accomplished by adding gypsum plaster to the mix and permitting it to set, thus stabilizing the bubbles. In fact, there is probably no successful bubble process that does not use some stabilizing method, either plaster or a flocculent;[123] and for this reason, it is difficult, because of the fluxing elements added, to make high-temperature insulating firebrick by the bubble process.

A high porosity can also be obtained by adding to the mix an inorganic refractory material having itself a high porosity. Such materials include diatomaceous earth, bloated clay pellets, or porous grog.

Molding Methods. The molding of the insulating firebrick mixes is not particularly difficult, as the mixtures containing organic matter can be readily molded by the soft-mud method, whereas the bubble method is best carried out by pouring the slip into molds until the mass has set. Use of the stiff-mud or dry-press method for these highly porous materials is difficult; for if they contain organic matter, they are usually rather elastic and difficulties from pressure cracking are troublesome. On the other hand, if the bubble process is used, any considerable amount of pressure would squeeze the air out of the structure and the density would be too high.

Chesters[126] *et al.* describe the forming of basic insulating brick.

TABLE 23. USE OF WEAR-RESISTING METALS

	Pug knives	Auger dies	Muller tires	Dry-press pads	Dry-press liners
"Ni-hard"					
High-chrome steel				×	
White cast iron		×	×		
Tool steel				×	×
Stellited steel				×	×
Tungsten carbide		×			
Chrome moly steel (heat-treated)			×		

8. Abrasion-resisting Metals. In the stiff-mud and dry-press process previously mentioned, numerous metal parts receive considerable wear as

a result of the abrasive action of the grog particles in the mix. These parts include the mullers of the wet and dry pan, the blades of pug mills and augers, auger dies, and the die boxes of re-presses and dry presses. Table 23 gives a summary of a number of wear-resisting metals that have been used.[86] There is, however, at present no great uniformity in the use of these materials, as some plants will obtain better life with one and some plants with another, owing, perhaps, to the differences in their mixes. A great deal of development work is still to be done in this field.

Dry-press and re-press die wear depends greatly on the mix. One hundred million bricks can be produced from plastic and flint clay in a set of liners; but when high-grog clay bricks or highly burned magnesite or chrome are used, the life may drop to as low as 5,000 bricks.

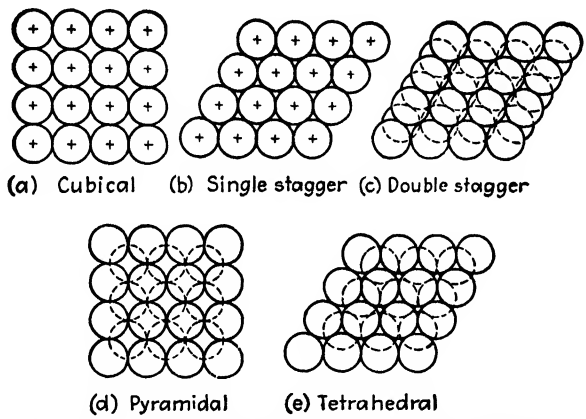


FIG. 78. Various methods of packing spherical particles.

9. Grog Sizing. The manufacturer of refractories is coming more and more to realize the importance of maintaining consistency of particle sizes of the grog or flint clay portion of his mix, especially where he has to make a low-porosity or low-shrinking refractory or an unburned refractory with a chemical bond. It has also been found that proper sizing helps the spalling resistance. Some manufacturers are going so far as to divide their particles by screens into a series of size fractions and then are recombining them by definite weights to produce the desired distribution. Others control size by proper adjustments of screens and crushers.

If the one-component system is considered first, *i.e.*, particles having a single diameter, it will be found that the closeness of packing depends on the arrangement of particles and their shapes. Taking the simplest case, *i.e.*, spheres, there are five different methods of packing, which are shown in Fig. 78 and the results given in Table 24.

In the case of irregular particles as would be obtained from a crusher, the packing varies between 40 and 50 per cent, although theoretically, with perfectly arranged cubes, the voids would be zero.

TABLE 24. VOIDS WITH DIFFERENT METHODS OF PACKING[128]

Type of packing of spheres, in Fig. 78	Voids, per cent
Cubical	47.64
Single stagger (cubical tetrahedral)	39.55
Double stagger	30.20
Pyramidal	25.95
Tetrahedral	25.95

Consider next, the two-component system wherein a coarse grain and a fine grain are mixed and shaken down to the minimum volume; the clearest picture of the situation can be obtained by referring to the packing diagram of Westman[128,139] shown in Fig. 79. Along the base is plotted the

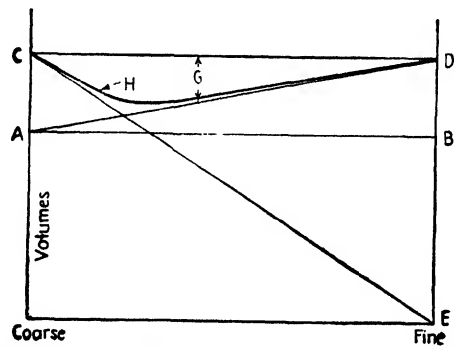


FIG. 79. Packing diagram for two sizes of particles.

proportion of coarse and fine in the mix, giving a constant total weight. On the vertical scale are plotted volumes. A line AB represents the true volume of the mixture. Point C represents the apparent volume of the coarse mix, and D the apparent volume of the fine mix, the apparent volume being the true volume plus the volume of voids. Now suppose that a small proportion of the coarse material is replaced by fine material. It is obvious that up to a certain point, the fines will simply fill the voids between the larger grains and therefore the total apparent volume will decrease in proportion to the amount of fines added. Accordingly, the theoretical apparent volume will follow the curve CE. Now starting from the other end of the diagram, if a certain amount of the fine material is replaced by the coarse, the coarse material will displace an equal volume of fine material and the voids existing in the fines. Therefore the total volume will decrease owing to an elimination of a portion of the voids in

the finer material. Consequently, the line AD will represent the theoretical apparent volumes. Where the lines CE and AD cross will be the minimum volume from a mixture of coarse and fine having an infinite ratio between the diameters. Actually, however, we have a finite ratio, and the actual curve of apparent volume will be indicated by H. The line CD is the apparent volume of the fractions before mixing, and the distance G represents the shrinkage in volume during the mixing process.

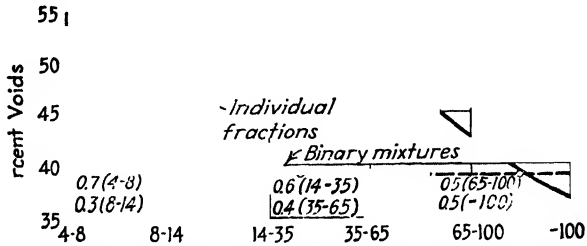


FIG. 80. Porosity diagram for crushed kaolin grog; individual fractions and binary mixtures. (*J. Am. Ceram. Soc.*)

Results obtained on crushed kaolin grog are given in Fig. 80 where are shown individual screened fractions and binary mixtures of these fractions mixed to give the densest packing.

When we come to systems of three components, the apparent volume can be indicated by surfaces. It will be found, however, that from practical considerations, little is gained by using more than two or three components in the mixture because of the impossibility of getting large-

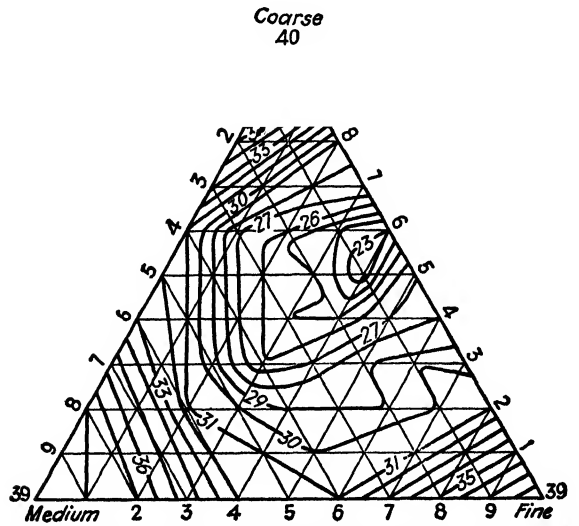


FIG. 81. Porosity diagram for crushed kaolin grog; ternary mixtures. (*J. Am. Ceram. Soc.*)

diameter ratios between the successive sizes. Figure 81 shows a three-component diagram for the crushed kaolin grog of Fig. 80. The densest mix has a proportion of 40 per cent fine, 50 per cent coarse, and 10 per cent medium, giving a porosity of 22 per cent.

10. Chemical Bonding. A great deal of interest has been shown recently in refractories that are chemically bonded with a setting material, which gives to the brick sufficient mechanical strength so that it can be used in the furnace without previous burning. In order to do this, it is necessary to have a large proportion of well-fired nonplastic material in the brick and have it sized in such a way as to give a very dense packing. In addition, the bricks must be pressed under high enough pressure to reduce the voids as far as possible. Bricks of this type have been made of magnesite, chrome, and fireclays.

One type of bond consists of magnesium chloride or magnesium oxychloride, used generally with a magnesite or chrome base. The patent of France[144,145] is typical of this type. Another bond is phosphoric acid, which has been used with a zirconia base according to the patent of Morgan[151,158] and with an aluminous material in the patent of Hood.[153] Bonds have also been suggested, such as silicate of soda[149] and a soluble aluminum salt, according to the patent of Betts.[148] However, one difficulty with the use of soluble salts is their migration to the surface on drying.

A great many organic types of bonds have been suggested. A synthetic resin bond is indicated in the patent of Danchower,[146] and Schwartzwalder[157] suggests the use of bakelite. Aluminum formate is used for bonding silica-alumina materials by Rohde.[161] Methyl silicate has also been suggested in a number of occasions as a bond for silica-alumina refractories, since a colloidal silica having considerable strength is precipitated. Other organic materials such as linseed oil and sulfide waste liquor[159] have been suggested. For lower temperature refractories, it is possible to use a high-alumina cement.

In looking over the list of bonds, it will be noted that many of them are at present too expensive for use anywhere except in laboratory-type refractories. Others have some practical difficulties; *e.g.*, the phosphoric acid is so hydroscopic and so hazardous to the health of workmen that it has operating difficulties. Probably the most useful bonds at present are the magnesium oxychloride, sulfate waste, and high-alumina cement.

The chemically bonded refractories in some types of service give results superior to the burned refractories, especially in resistance to spalling; consequently, they have definitely taken a place in our refractory production. Of course, the first thought on considering this type of refractory is the great saving in firing cost; but when the problem is analyzed, it is

usually found that with the additional cost of the bond and the necessity for carefully sizing the nonplastic, which comprises practically the whole brick, the total cost is little, if any, less than for the burned brick.

11. Hot Molding. The suggestion has been put forth from time to time of producing refractories by pressing the heated refractory material in the mold so that the bonding would take place by welding together the particles while they were sufficiently hot to have a certain amount of glass in the viscous condition. Such a method is suggested in the patent of Duffield.[166] Many experimenters have shown that a comparatively strong brick can be made at a temperature much below the burning temperature if pressure is exerted. However, this attractive process of molding refractories has not proved commercially successful because of the great difficulty in providing molds that will operate at the high temperatures necessary and still give a reasonable amount of life. Special refractories such as boron carbide are hot pressed, a process described in Chap. VIII.

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CHAPTER VII

DRYING

1. The Mechanism of Drying. The work of Sherwood[4,5,8] and his collaborators has done much to give a clear picture of the drying process in porous solids. It is logical to divide the drying into two periods: the constant-rate period and the falling-rate period.

The Constant-rate Period. At the start of the drying process, when the clay contains enough water at least to fill the pores, there will be a continuous film of water over the surface particles, as evidenced by the comparatively dark color of the wet clay. It is therefore not unexpected to find that the rate of drying per unit area of surface is substantially the same as for a free water surface. This rate in terms of temperature, humidity, and velocity of the air is shown in Fig. 82. As the drying proceeds at this rate, it is obvious that water must travel through the pores toward the surface to supply the evaporation loss. In all but exceptional cases, where the drying rate is very high or the clay very fine grained, the water will travel by capillary forces as fast as it is carried away. In the case of clay, the piece will shrink in volume equivalent to the volume of water lost until the particles touch, and thereafter air must enter the pores to take the place of the water. Soon after this happens, it will be found that the water cannot travel to the surface fast enough to maintain an unbroken surface film; so the drying rate starts to decrease. This rather sharply defined point may be called the "critical point" and corresponds approximately to cessation of shrinkage.

It might be thought that a nonshrinking material like sand and water would not show any constant-rate period because the pores would start to empty at once. Experiments show this to be true when the particles are fine; but when the particles are coarse, the resistance to flow is so slight that even with air in the pores, the surface drying rate is the governing factor. This is shown clearly in Fig. 83 for a fine and coarse sand.

The Falling-rate Period. Beyond the critical point, the drying rate is governed by the rate of transfer of water from the interior to the surface and rapidly becomes less as the drying proceeds. It is believed that beyond the critical point, the continuous surface film is broken and the water surface recedes into the capillaries, giving the light color to the clay at this stage. As the drying proceeds, more and more of the water is converted

inside the structure into vapor, making it necessary for this to travel out through the nearly empty capillaries to the surface.

In Fig. 84, an attempt has been made to show how an enlarged section of the clay would look at various stages of the drying process. In *A*, the

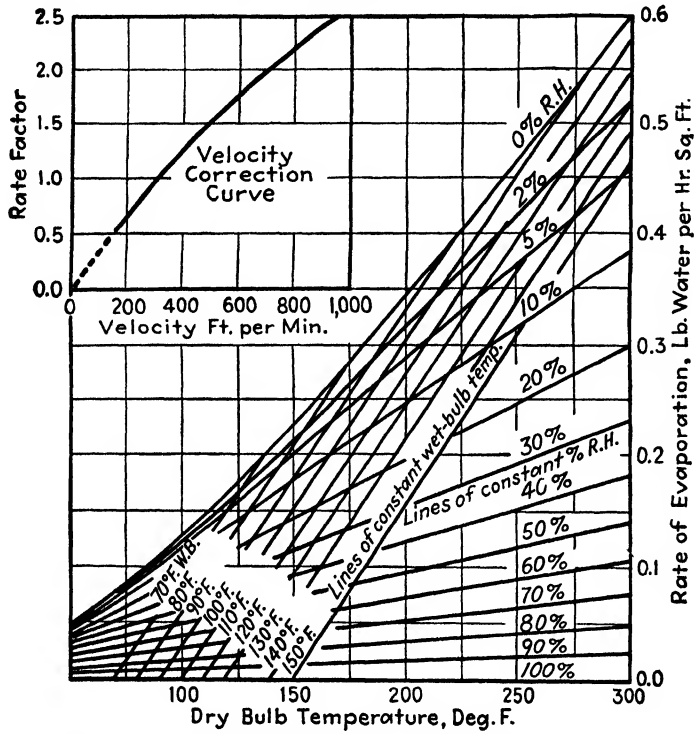

FIG. 82. Evaporation chart for free water surface. (*C. B. Shepherd, C. Hudlock, and R. C. Brewer, Industrial and Engineering Chemistry*, 1938.)

clay particles are well separated by a water film, which also runs continuously over the surface. In *B*, the amount of water has decreased until the particles touch one another, but there is still a continuous surface film. In

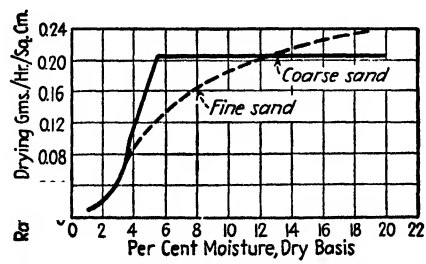

FIG. 83. Drying rates of sand-water mixes, (*After Sherwood.*)

C, the water has decreased until the surface layer is broken and the level recedes into the capillaries with some air in the structure. Water is brought to the surface by a capillary flow and as vapor. In *D*, the water has still further decreased until it is found only in a few places where the particles

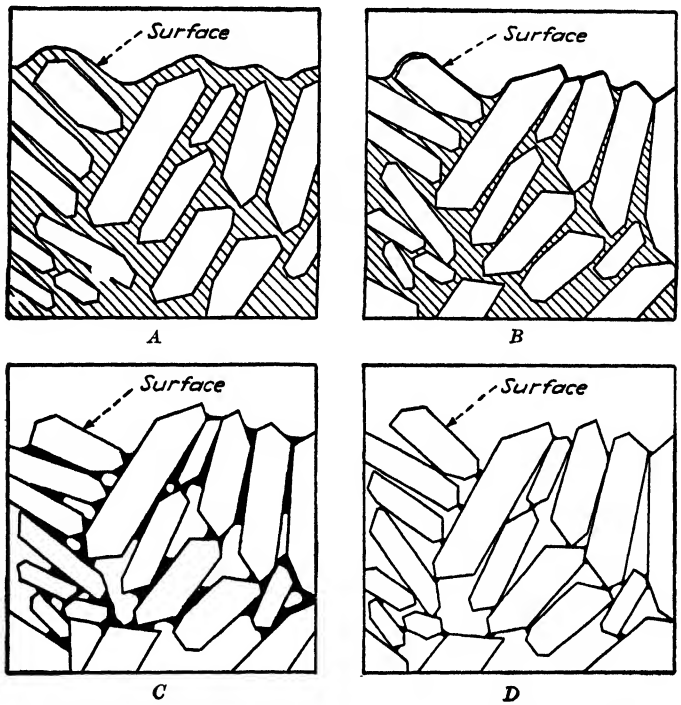

FIG. 84. Enlarged section drawings of clay at various stages of drying.

come closest together. Here all the transfer of water is in the form of vapor. These four conditions are shown on the typical drying-rate curve for a clay in Fig. 85.

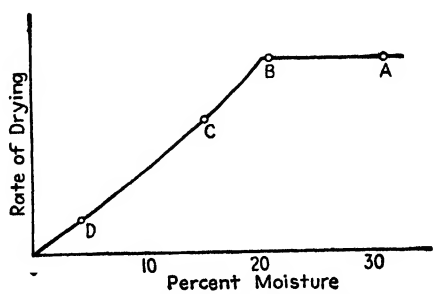

FIG. 85. A typical drying-rate curve for a clay.

The last of the water comes off slowly because it is adsorbed on the surface of the dry particles. Practically, however, it is never necessary to remove the last trace of water. In fact, a bone-dry piece is apt to be brittle and hard to handle.

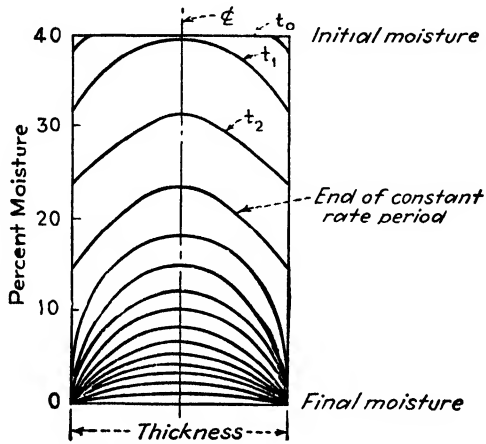

FIG. 86. The moisture distribution across a slab of drying clay.

Moisture Gradient in Clay Body. The moisture distribution across a slab of drying clay may be shown to follow the lines in Fig. 86. At the critical point, the moisture at the surface drops rapidly toward zero. In the constant-rate period, however, the curves are parallel and may be expressed mathematically by Newton's law of diffusion

$$\frac{\delta M}{\delta \theta} = K \frac{\delta^2 M}{\delta x^2}$$

in the same way as for heat flow. Here

M = the moisture concentration per unit volume
θ = the time
x = the distance from the surface
K = a constant

The solution of this equation and its application to the constant-rate period has been carried out by Gilliland and Sherwood,[10] which permits the calculation of the moisture distribution in a slab after any time interval. Reference should be made to the original papers for a full discussion of this calculation.

2. Drying Shrinkage. The drying shrinkage of a clay or body is an important characteristic because it largely governs the maximum safe rate of drying. The drying-shrinkage curve is also very helpful in studying some phases of the clay-water system.

Mechanism of Drying Shrinkage. The mechanism of shrinkage is a very simple one. If the volume shrinkage is plotted against the volume of water in the clay, as in Fig. 87, it will be seen that the shrinkage curve is a straight line with a 45-deg slope. In other words, the volume shrinkage is just equal to the volume of water lost in drying down to the critical point, where the interparticle film becomes so thin that the particles touch one another and shrinkage can go no further. This will be made clearer by referring back to Fig. 84, which shows the condition of the clay and water at the points lettered on the curve of Fig. 87.

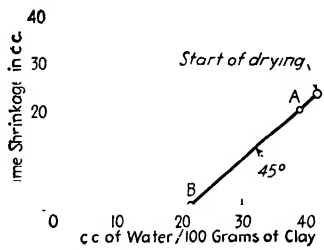

FIG. 87. Theoretical drying-shrinkage curve of clay.

The water lost from the clay in drying between its original condition and the critical point is often referred to as "shrinkage water," and the remainder as "pore water."

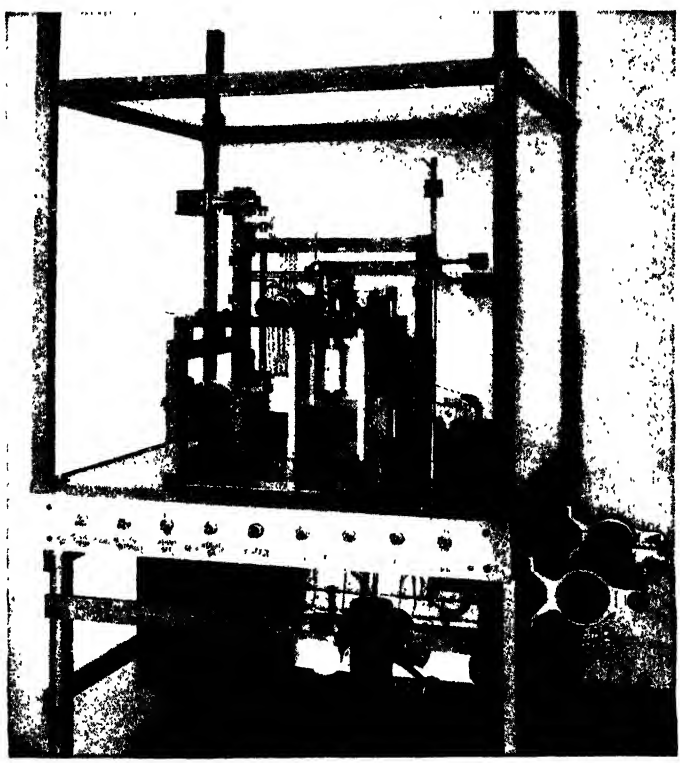

FIG. 88. Apparatus for determining drying shrinkage.

The critical point is not usually so sharply defined as shown in Fig. 87, nor does the lower end of the shrinkage curve always lie along the axis. When clays of the swelling type, such as bentonite, are present, the curve is above the axis and only shrinks the final amount just before dryness, because of the fact that the last of the water is more firmly held between the crystal layers than on the surface of the particles. Other clays have shrinkage curves falling below the axis as a result, at the end of the drying process, of a slight expansion that has not yet been explained but is perhaps due to the opening up of kaolinite books on losing the last trace of water.

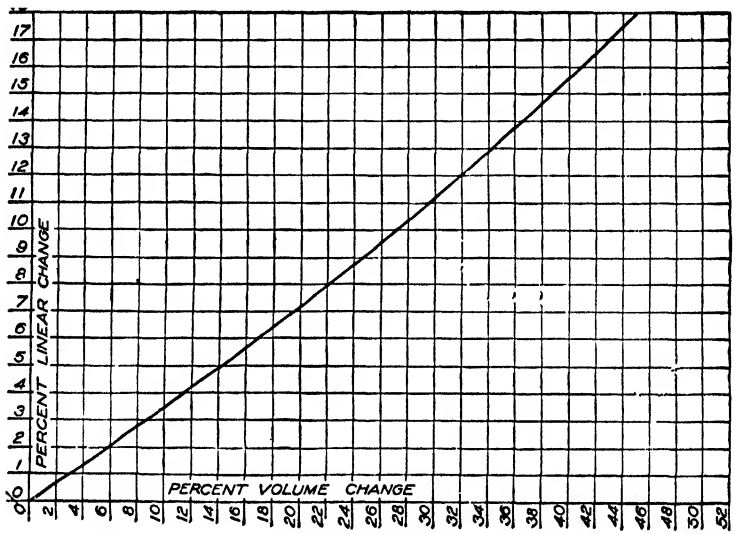

FIG. 89. Curve for the conversion of volume to linear shrinkage based on initial dimensions.

Measurement of Drying Shrinkage. Shrinkage can be measured by either a length change or a volume change. The former is more useful for studying the type of shrinkage curve, whereas the latter gives more accurately the over-all shrinkage.

The apparatus[24] shown in Fig. 88 is a convenient one for obtaining shrinkage curves. The test specimen is in the form of a hollow cylinder $\frac{7}{8}$ in. outside diameter, 2 in. long, with a $\frac{1}{8}$-in. wall. It is placed on an automatic balance in a chamber with controlled humidity and temperature; accordingly the change in length can be precisely determined with a micrometer telescope.

Volume shrinkage is usually measured by placing the specimen, at various stages of dryness, in a mercury volumeter. Volume shrinkage can be converted to linear shrinkage by the curve in Fig. 89 or by Tables 25 and 26.

TABLE 25

Four-figure table for converting:

1. Volume drying shrinkage (percentage of plastic volume) to linear drying shrinkage (percentage of plastic length).

2. Volume of firing shrinkage (percentage of unfired or dry volume) to linear firing shrinkage (percentage of unfired or dry length).

3. Volume of expansion (percentage of final volume) to linear expansion (percentage of final length).

(Courtesy of Dr. A. E. R. Westman, American Ceramic Society)

Percentage volume change	Percentage volume change										Differences
	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	
	Percentage linear change										
0	0.000	0.033	0.067	0.100	0.134	0.167	0.200	0.234	0.267	0.301	0.034
1	0.334	0.368	0.402	0.435	0.469	0.503	0.536	0.570	0.604	0.638	0.034
2	0.672	0.705	0.739	0.773	0.806	0.840	0.874	0.908	0.942	0.976	0.034
3	1.010	1.044	1.078	1.112	1.146	1.181	1.215	1.249	1.283	1.317	0.034
4	1.352	1.386	1.420	1.455	1.489	1.523	1.558	1.592	1.626	1.661	0.034
5	1.695	1.730	1.764	1.799	1.834	1.868	1.903	1.937	1.972	2.007	0.035
6	2.041	2.076	2.111	2.146	2.181	2.216	2.251	2.285	2.320	2.355	0.035
7	2.390	2.425	2.460	2.495	2.530	2.565	2.600	2.636	2.671	2.706	0.035
8	2.741	2.776	2.812	2.847	2.882	2.918	2.953	2.988	3.023	3.059	0.035
9	3.095	3.130	3.166	3.201	3.237	3.273	3.308	3.344	3.380	3.415	0.036
10	3.451	3.487	3.523	3.559	3.594	3.630	3.666	3.702	3.738	3.774	0.036
11	3.810	3.846	3.882	3.918	3.954	3.990	4.027	4.063	4.099	4.135	0 036
12	4.172	4.208	4.244	4.281	4.317	4.354	4.390	4.426	4.463	4.500	0.036
13	4.536	4.572	4.609	4.646	4.683	4.719	4.756	4.793	4.830	4.866	0.037
14	4.903	4.940	4.977	5.014	5.051	5.088	5.125	5.162	5.199	5.236	0.037
15	5.273	5.310	5.348	5.385	5.422	5.459	5.497	5.534	5.571	5.609	0.037
16	5.646	5.684	5.721	5.759	5.797	5.834	5.872	5.909	5.947	5.984	0.037
17	6.022	6.060	6.098	6.136	6.174	6.212	6.249	6.287	6.325	6.363	0.038
18	6.401	6.439	6.477	6.515	6.553	6.592	6 630	6.638	6.706	6.745	0.038
19	6.783	6.822	6.860	6.899	6.937	6.975	7.014	7.052	7.091	7.130	0.038
20	7.168	7.207	7.246	7.284	7.323	7.362	7.401	7.440	7.479	7.518	0.039
21	7.557	7.596	7.635	7.674	7.713	7.752	7.791	7.831	7.870	7.909	0.039
22	7.949	7.988	8.027	8.067	8.106	8.146	8.185	8.225	8.265	8.304	0.039
23	8.344	8.383	8.423	8.463	8.503	8.543	8.582	8.622	8.662	8.702	0.040
24	8.742	8.782	8.822	8.862	8.903	8.943	8.983	9.023	9.063	9.104	0.040
25	9.144	9.184	9.225	9.265	9.306	9.346	9.387	9.428	9.468	9.509	0.040
26	9.550	9.590	9.361	9.672	9.713	9.754	9.795	9.836	9.877	9.918	0.040
27	9.959	10.00	10.04	10.08	10.12	10.16	10.21	10.25	10.29	10.33	0.040
28	10.37	10.41	10.45	10.50	10.54	10.58	10.62	10.66	10.71	10.75	0.040
29	10.79	10.83	10.87	10.91	10.96	11.00	11.04	11.08	11.13	11.17	0.040
30	11.21	11.25	11.29	11.34	11.38	11.42	11.46	11.51	11.55	11.59	0.040
31	11.63	11.68	11.72	11.76	11.81	11.85	11.89	11.93	11.98	12.02	0.040
32	12.06	12.11	12.15	12.19	12.23	12.28	12.32	12.37	12.41	12.45	0.040
33	12.50	12.54	12.58	12.63	12.67	12.72	12.76	12.80	12.85	12.89	0.040
34	12.93	12.97	13.02	13.07	13.11	13.15	13.20	13.24	13.29	13.33	0.040
35	13.38	13.42	13.47	13.51	13.55	13.60	13.64	13.69	13.74	13.78	0.040
36	13.82	13.87	13.91	13.96	14.00	14.05	14.09	14.14	14.18	14.23	0.040
37	14.27	14.32	14.36	14.41	14.46	14.50	14.55	14.59	14.64	14.68	0.050
38	14.73	14.78	14.82	14.87	14.91	14.96	15.01	15.05	15.10	15.14	0.050
39	15.19	15.24	15.28	15.33	15.38	15.42	15.47	15.52	15.56	15.61	0.050
40	15.66	15.70	15.75	15.80	15.84	15.89	15.94	15.99	16.03	16.08	0.050
41	16.13	16.18	16.23	16.27	16.32	16.37	16.41	16.46	16.51	16.56	0.050
42	16.60	16.65	16.70	16.75	16.80	16.84	16.89	16.94	16.99	17.04	0.050
43	17.09	17.14	17.18	17.23	17.28	17.33	17.38	17.43	17.48	17.53	0.050
44	17.57	17.62	17.67	17.72	17.77	17.82	17.87	17.92	17.97	18.02	0.050
45	18.07	18.12	18.17	18.22	18.27	18.32	18.37	18.42	18.47	18.52	0.050
46	18.57	18.62	18.67	18.72	18.77	18.82	18.87	18.92	18.97	19.02	0.050
47	19.07	19.12	19.18	19.23	19.28	19.33	19.38	19.43	19.48	19.53	0.050
48	19.59	19.64	19 69	19.74	19.79	19.84	19.90	19.95	20.00	20.05	0.050
49	20.10	20.16	20.21	20.26	20.31	20.37	20.42	20.47	20.52	20.58	0.050
50	20.63	20.68	20.74	20.79	20.84	20.90	20.95	21.00	21 06	21.11	0.050

TABLE 26

Four-figure table for converting:

1. Volume of drying shrinkage (percentage of dry volume) to linear drying shrinkage (percentage of dry length).

2. Volume of firing shrinkage (percentage of fired volume) to linear firing shrinkage (percentage of fired length).

3. Volume of expansion (percentage of initial volume) to linear expansion (percentage of initial length).

(Courtesy of Dr. A. E. R. Westman, American Ceramic Society)

Percentage volume change	Percentage volume change										Differences
	0 0	0 1	0 2	0.3	0.4	0.5	0 6	0.7	0.8	0 9	
	Percentage linear change										
0	0.000	0.033	0.067	0.100	0.133	0.166	0.200	0.233	0.266	0.299	0 033
1	0.332	0.365	0.398	0.431	0.464	0.497	0.530	0.563	0.596	0.629	0.033
2	0.662	0.695	0.728	0.761	0.794	0.826	0.859	0.892	0 925	0.957	0.033
3	0.990	1.023	1.055	1.088	1.121	1.153	1.186	1.218	1.251	1.283	0.033
4	1.316	1.348	1.381	1.413	1.446	1.478	1.510	1.543	1.575	1.607	0.032
5	1.640	1.672	1.704	1.736	1.769	1.801	1.833	1.865	1.897	1.929	0.032
6	1.961	1.993	2.025	2.057	2.089	2.121	2.153	2.185	2.217	2.249	0.032
7	2.281	2.313	2.345	2.376	2.408	2.440	2.472	2.503	2.535	2.567	0.032
8	2.599	2.630	2.662	2.693	2.725	2.757	2.788	2.820	2.851	2.883	0 032
9	2.914	2.946	2.977	3.009	3.040	3.071	3.103	3.134	3.165	3.196	0.031
10	3.228	3.259	3.291	3.322	3.353	3.384	3.415	3.446	3.478	3.509	0.031
11	3.540	3.571	3.602	3.633	3.664	3.695	3.726	3.757	3.788	3.819	0 031
12	3.850	3.881	3.912	3.943	3.973	4.004	4.035	4.066	4.097	4.127	0.031
13	4.158	4.189	4.219	4.250	4.281	4.311	4.342	4.373	4.403	4.434	0.031
14	4.464	4.495	4.525	4.556	4.586	4.617	4.647	4.678	4.708	4.739	0.030
15	4.769	4.799	4.830	4.860	4.890	4.921	4.951	4.981	5.011	5.042	0.030
16	5.072	5.102	5.132	5.162	5.192	5.222	5.253	5.283	5.313	5.343	0.030
17	5.373	5.403	5.433	5.463	5.493	5.523	5.553	5.583	5.612	5.642	0.030
18	5.672	5.702	5.732	5.762	5.791	5.821	5.851	5.881	5.910	5.940	0 030
19	5.970	6.000	6.029	6.059	6.088	6.118	6.148	6.177	6.206	6.236	0.030
20	6.266	6.295	6.325	6.354	6.384	6.413	6.443	6.472	6.501	6.531	0.029
21	6.560	6.590	6.619	6.648	6.678	6.707	6.736	6.765	6.795	6.824	0.029
22	6.853	6.882	6.911	6.940	6.970	6.999	7.028	7.057	7.086	7.115	0.029
23	7.144	7.173	7.202	7.231	7.260	7.289	7.318	7.347	7.376	7.405	0 029
24	7.434	7.463	7.491	7.520	7.549	7.578	7.607	7.635	7.664	7.693	0 029
25	7.722	7.750	7.779	7.808	7.836	7.865	7.894	7.922	7.951	7.980	0.029
26	8.008	8.037	8.065	8.094	8.122	8.151	8.179	8.208	8.236	8.265	0.028
27	8.293	8.322	8.350	8.378	8.407	8.435	8.463	8.492	8.520	8.548	0.028
28	8.577	8 605	8.633	8.661	8.690	8.718	8.746	8.774	8.802	8.831	0 028
29	8.859	8.887	8.915	8.943	8.971	8.999	9.027	9.055	9.083	9.111	0.028
30	9.139	9.167	9.195	9.223	9.251	9.279	9.307	9.335	9.363	9.391	0.028
31	9.418	9.446	9.474	9.502	9.530	9.557	9.585	9.613	9.641	9.668	0.028
32	9.696	9.724	9.751	9.779	9.807	9.834	9.862	9.890	9.917	9.945	0.027
33	9.972	10.00	10.02	10.05	10.08	10.11	10.14	10.16	10.19	10.22	0.030
34	10.25	10.27	10.30	10.33	10.36	10.38	10.41	10.44	10.47	10.49	0.030
35	10.52	10.55	10.58	10.60	10.63	10.66	10.68	10.71	10.74	10.77	0.030
36	10.79	10.82	10.85	10.87	10.90	10.93	10.96	10.98	11.00	11.03	0.030
37	11.06	11.09	11.12	11.14	11.17	11.20	11.23	11.25	11.28	11.31	0.030
38	11.33	11.36	11.39	11.41	11.44	11.47	11.49	11.52	11.55	11.57	0.030
39	11.60	11.63	11.65	11.68	11.71	11.74	11.76	11.79	11.82	11.84	0.030
40	11.87	11.90	11.92	11.95	11.98	12.00	12.03	12.05	12.08	12.11	0.030
41	12.13	12.16	12.19	12.21	12.24	12.27	12.29	12.32	12.35	12.37	0.030
42	12.40	12.43	12.45	12.48	12.50	12.53	12.56	12.58	12 61	12.64	0.030
43	12.66	12.69	12.71	12.74	12.77	12.79	12.82	12.85	12.87	12.90	0.030
44	12.92	12.95	12.98	13.00	13.03	13.05	13.08	13.11	13.13	13.16	0.030
45	13.19	13.21	13.24	13.26	13.29	13.31	13.34	13.37	13.39	13.42	0.030
46	13.44	13.47	13.50	13.52	13.55	13.57	13.60	13.62	13.65	13.68	0.030
47	13.70	13 73	13.75	13.78	13.81	13.83	13.86	13.88	13.91	13.93	0.030
48	13.96	13 99	14.01	14.04	14.06	14.09	14.11	14.14	14.17	14.19	0.030
49	14.22	14.24	14.27	14.29	14.32	14.34	14.37	14.39	14.42	14.44	0.030
50	14.47	14.50	14.52	14.55	14.57	14.60	14.62	14.65	14.67	14.70	

Water-film Thickness. The ceramist is much interested in the thickness of the water film separating the clay particles. If the total linear shrinkage and the number of films per unit length are known, this factor can be readily calculated. The total shrinkage can be easily determined, but the number of films is more difficult to estimate. The most recent work on this subject is by Norton and Johnson[15] who measured the drying shrinkage of a number of monodisperse size fractions of a kaolin. Provided the size and shape of the particles are known, the number of films are readily computed. In this way, they found a value of about 0.005 μ as the film thickness in a plastic mass, or a layer of about 50 water molecules. This value can also

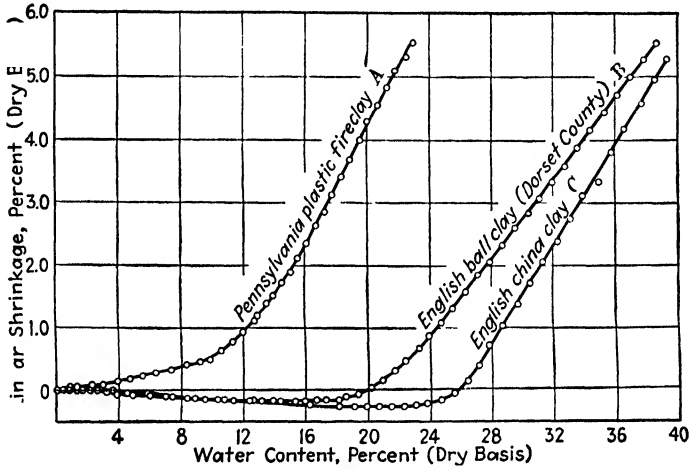

FIG. 90. Drying-shrinkage curves of typical clays.

be computed by determining the thickness of the shrinkage water when spread over an area equal to the surface area of the particles. The result is of the same order of magnitude.

Shrinkage Curves. Figure 90 illustrates drying-shrinkage curves for a few typical clays. Curve *A* for a fireclay gives the typical secondary shrinkage, and curves *B* and *C* show a slight expansion.

3. Dry Strength. The dry, or "green," strength of clays is a unique and more or less unexplained property. Such theories as postulate molecular cohesion, felting of the particles, or organic colloids are not entirely substantiated as yet. It is known that the dry strength increases as the area of the particles increases (finer particles). Also the strength increases with more of some adsorbed ions. For example, a kaolin having a strength (modulus of rupture) of 400 psi when dialyzed showed an increase to 1,000 psi when saturated with sodium ions. These facts indicate that strength is due, at least in part, to attractive forces between the clay mineral crystals. This is an excellent field for further research.

4. Factors Influencing Drying Efficiency. When clayware is dried, the operation must be carried out as rapidly as possible in order to cut down the size and cost of the drying equipment. Great strides have been made in the last ten or fifteen years in increasing the speed and efficiency of drying by means of controlled humidity driers.

Maximum Drying Rate. The maximum drying rate is determined by the stresses set up in the ware and the ability of the body to resist them. The same factors apply as will be discussed in Chap. XV for spalling. The

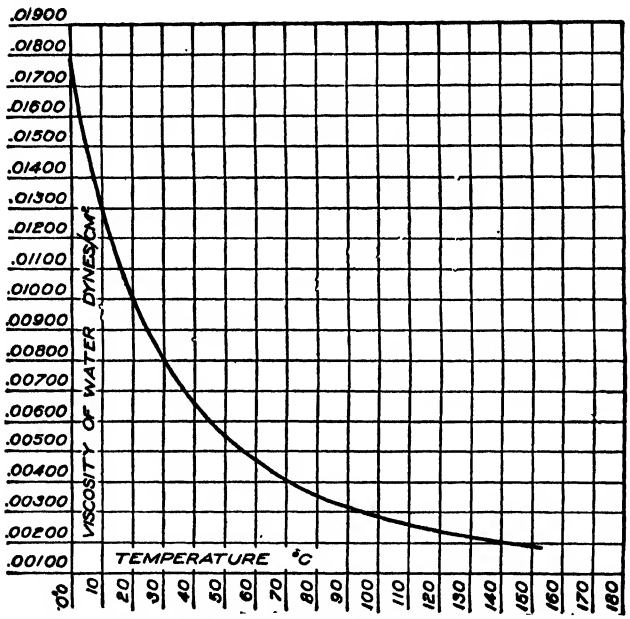

FIG. 91. The variation of the viscosity of water with temperature.

tendency to crack for similar-sized pieces is a function of the moisture gradient, the slope of the shrinkage curve, and the flexibility of the structure. The only variable that can be controlled in the drying operation is the moisture gradient; and for a given rate of drying, this can be decreased only by reducing the viscosity of the water flowing through the capillaries. The viscosity of water decreases quite rapidly with temperature, as shown in Fig. 91, which explains the reason why, in modern driers, the ware is heated rapidly to the maximum temperature in a saturated atmosphere before much drying takes place.

The size of the refractory piece influences the time required to dry. Macey[13] has shown that under constant drying conditions, various sizes of cubes dry in times proportional to the length of the edge of the cube.

Also the larger the piece the greater will be the tendency to crack under given drying conditions. It should also be realized that when the water content is sufficiently low to come below the critical point, the shrinkage stops and therefore the drying can be carried on as rapidly as desired, provided the vapor can escape from the interior without setting up a bursting pressure.

Examples of Drying. As a concrete example, the problem of drying a brick as rapidly as possible when made from a mechanically weak, high-shrinking clay will be considered. In order to prevent too rapid surface evaporation, no artificial velocity was imparted to the air and the humidity

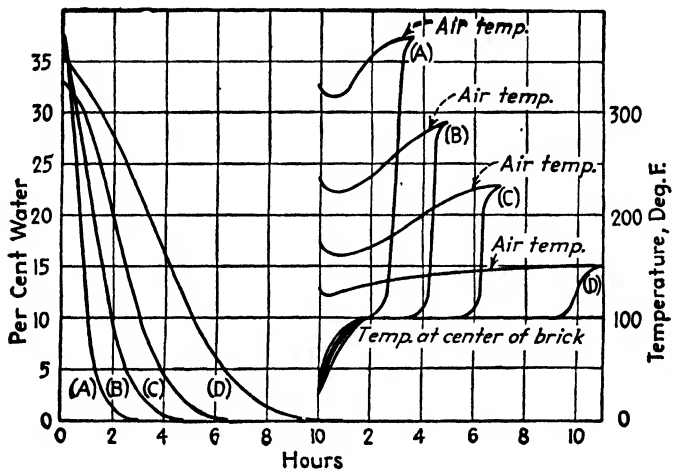

FIG. 92. Curves showing the rate of drying of bricks under various temperature conditions.

was kept at a maximum. It was then necessary only to find the maximum temperature that could be used without cracking the brick. It should be realized that if the brick could be heated uniformly and at a rapid rate, the drying could proceed with extreme rapidity because of the high diffusion rate at elevated temperatures. However, it takes some time for the center of the brick to reach the temperature of the surface, and the resultant temperature gradient will, of course, increase the moisture gradient, which, as explained before, is the limiting factor in the rate of drying.

The apparatus used for the experiments consisted of a closed chamber with the brick suspended on a platform in the center of it. The heat was supplied by an electric heating coil so that any desired temperature could be easily obtained. The chamber, in each case, was brought up to the desired temperature, and the wet, cold brick was put in. Arrangements were made to obtain the weight of the brick continuously throughout the drying process. Figure 92 shows the curves for the rate of drying for

various temperature conditions. A brick dried under condition *D* showed no signs of cracking. Under condition *C*, a few slight cracks appeared on the surface; whereas under conditions *A* and *B*, the bricks were quite badly cracked.

Distribution of Heat. It is quite a step from drying a single brick in the laboratory to drying a full car in a production drier. Circulation of air must be adjusted both to bring heat to the brick at the required rate and, at the same time, to carry away the water vapor. In order to dry all the bricks alike, a large volume of air must be circulated with the proper distribution of velocity.

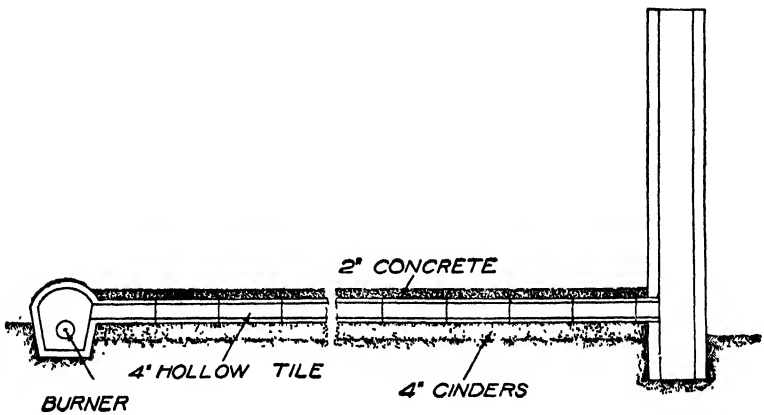

FIG. 93. Section showing construction of a direct-fired hot floor.

Conservation of Heat. A definite amount of heat is required to evaporate the water; but in addition, heat must be supplied for the waste air leaving the drier, for the heat in the bricks, and for the loss through the drier walls. Therefore, an efficient drier will have a minimum volume of exit gases, by means of recirculation, and will have well-insulated walls.

5. Drier Calculations. It is not within the scope of this book to consider drier design, as this is well covered in more general treatises. However, it might be well to point out some of the principles involved. The heat content of the air supplied to the drier, between the entrance and exit temperatures, must be sufficient to provide for the heat required in the drying operation. Also the volume of the air passing through the drier must be so great that the moisture added to it will not bring it above the saturation point at the exit temperature (or temperature of the entering bricks).

6. Types of Driers. The hot floor is used to a considerable extent at the present time for drying and tempering soft-mud bricks and for drying large shapes. The heat is supplied by means of steam pipes running in

conduits or tiles just under the surface of a concrete floor. The temperature of the floor can be controlled by valves, and the floor is usually divided up into small sections so that the temperature can be regulated according to the material drying at any particular point on the floor. Hot floors are sometimes heated by waste heat from the kilns or by direct heat from coal or oil fires, from which the hot gases pass under the floor in tile flues as shown in Fig. 93. These methods, however, are not so satisfactory as steam heating, because it is difficult to control the temperature of the floor and because the temperature will vary considerably from one end of the

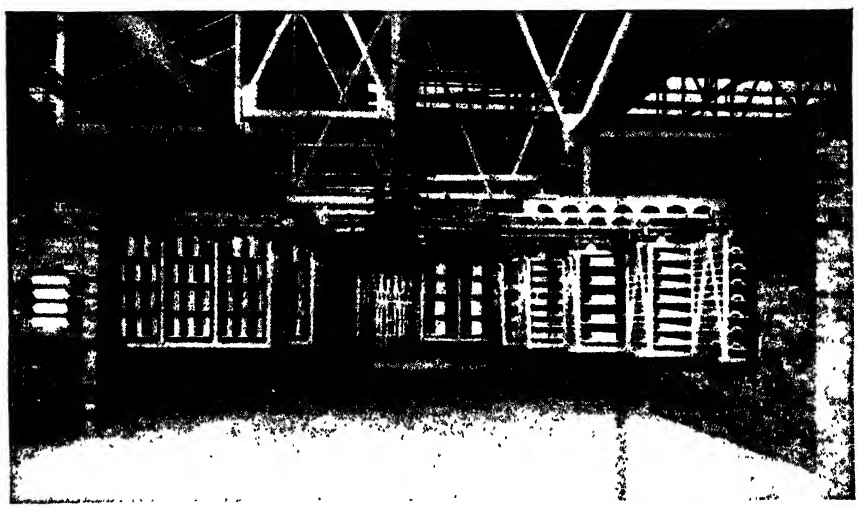

FIG. 94. A continuous drier with the ware on a monorail system. (*Courtesy of the A. P. Green Company.*)

floor to the other. Sometimes, the thickness of the floor is varied from the hot to the cold end to give a more even surface temperature. From one-half to four 9-in. equivalents can be dried per square foot of floor per 24 hr, depending on the clay, the water content, and the size. In some plants, one-half of the drier capacity is in the hot floor. Recently overhead unit heaters have been used to circulate air from above in order to increase the drying capacity per square foot.[48]

Tunnel driers are used mainly for bricks and small shapes. They consist of a long tunnel in which rack cars of bricks can be placed. Heat is supplied by steam coils under the tracks or, in some cases, by waste heat, which passes through the tunnel. The green bricks are usually pushed into the tunnel at the cooler end and gradually progress to the hotter end until they are completely dry. Figure 94 shows a tunnel of this type. The bricks or shapes are placed on shods that are held in the rack cars. Some-

times perforated shods are used to speed up the drying of the underside of the bricks. They cannot be used, however, with very soft clay, for they will mark the brick. Dry pressed brick are often dried directly on the tunnel kiln cars with a great saving in handling costs.

The more modern type of drier is the continuous-tunnel type, in which the loaded cars are pushed at a uniform rate through a tunnel having carefully regulated temperature and humidity values at each section. Fans or injectors are used to circulate the air around the steam coils and through the bricks in order to ensure a rapid and uniform transfer of heat to the

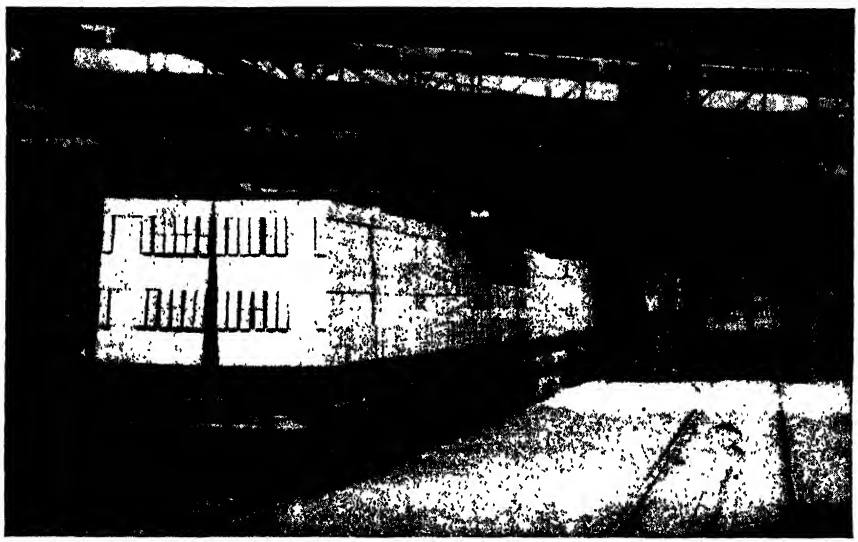

FIG. 95. The entrance to a humidity drier. (*Courtesy of the Harbison-Walker Refractories Company.*)

drying material. Usually recirculation is used; *i.e.*, the air is passed around a closed circuit, the only vent being a small escape pipe at the top of the tunnel to allow the moisture from the bricks to pass off. The tunnel is divided longitudinally into sections, and each section is controlled for temperature and humidity by automatic controllers. In general, the temperature and humidity are high at the start to heat the brick with little loss of water from the surface. The humidity is then gradually decreased as the bricks pass through the tunnel. The regulation, however, must be determined for the particular kind of clay being dried. Figures 95, 96, and 97 illustrate driers of this type and in Fig. 98 is shown a typical temperature schedule.[42]

The temperature in driers varies according to the nature of the clay and size of the articles. Generally it is kept as high as possible, 50°C (about

FIG. 96. The end of a continuous drier handling bricks on the tunnel kiln car. (*Courtesy of the Allied Engineering Corporation.*)

FIG. 97. Bricks from a tunnel drier being set on the tunnel kiln car. (*Courtesy of the Swindell-Dressler Corporation.*)

120°F) to 90°C (about 190°F). The capacity of a drier depends also upon the clay and the size of the articles. It is an economy to dry as rapidly as possible, as this reduces the investment in the drier, cars, and shods for a given output. Typical drying conditions are shown in Table 27. Infrared driers have been used in the ceramic industry for thin ware, but this principle has not as yet found much use in the refractories field.

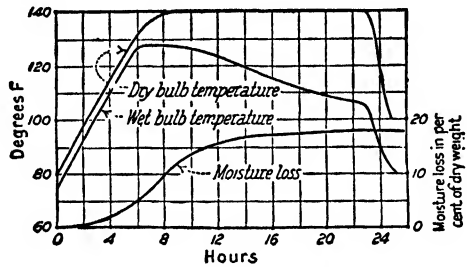

FIG. 98. A typical drying schedule for firebrick in a modern humidity drier. (*J. Am. Ceram. Soc.*)

Since the design and construction of efficient driers require considerable technical knowledge and experience, the amateur drier builder seldom turns out a satisfactory job. The scientific study of drying problems has lately resulted in great advances in this field. The following references should be consulted for the details of drier design.

TABLE 27. DRIER CONDITIONS

Type of brick	Maximum drier temperature		Time to dry 9-in. brick, hr.
	°F.	°C.	
Hand-molded	160	71	48
Stiff mud, re-pressed	160	71	24
Silica	150–250	66–121	24
Chrome and magnesite	180	82	16
Insulating firebrick	180	82	30

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CHAPTER VIII

THE FIRING OF CLAY AND OTHER REFRACTORY MATERIALS

1. Effect of Heat on Raw Clay. One of the most important steps in the manufacture of refractories is the firing process, whereby the raw clay is profoundly altered into a strong and partly vitreous mass. The steps occurring in the process are particularly important, as they guide us in the proper heat-treatment of a clay to give the greatest efficiency in firing and the most satisfactory finished product.

Methods of Measuring Heating Changes. The changes that occur in a clay on heating, though not at once evident, can be indirectly observed through a number of secondary alterations that can be detected by the proper type of measurement. One of the most obvious changes taking place in a heated clay is the loss in weight. This weight loss can be measured by placing a sample of clay in a constant-temperature furnace[24] and holding it at one temperature until the weight becomes constant, then increasing the temperature another step and holding it again, and so on until the clay loses no further weight. Also, the weight loss can be determined by raising the temperature of the sample at a predetermined rate and recording the weight of the specimen as a continuous function of time. The weight loss is due (1) to loss of adsorbed water at comparatively low temperatures, (2) to the loss of chemically combined water which occurs at a rather definite temperature for any particular clay mineral, and (3) loss of CO_2 and SO_2 from oxidation of carbon or the breaking up of carbonates and sulfides. The proper interpretation of the weight-loss curve of a clay will give a valuable insight into the clay constituents, as shown by the curves in Fig. 99 for a number of clay minerals. A well-crystallized mineral like kaolinite loses its chemical water substantially at one temperature, whereas an amorphous material like allophane loses it gradually.

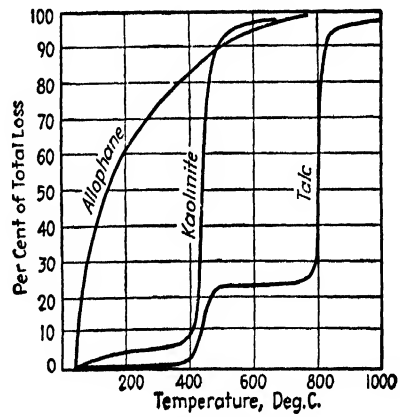

FIG. 99. Weight-loss curves.

Another characteristic of clay when heated is the absorption and evolution of heat[32] at certain temperatures, which can readily be determined by the differential thermal apparatus described in Chap. IV. A typical curve of this type for a fireclay containing only the mineral kaolinite is shown in Fig. 100. The slight heat absorption at 150°C (about 300°F) is due to the driving off of adsorbed water from the surface of the grains. The small heat evolution at approximately 400°C (about 750°F) is caused by the oxidation of a slight amount of organic matter in the clay. The larger absorption peak at 620°C (about 1150°F) is caused by the evolution of the chemically combined water in the kaolinite structure, and the sharp and high peak at 980°C (about 1800°F) is believed to be due to the change of amorphous alumina to the crystalline γ-form. The small peak at 1200°C (about 2190°F) is considered to be the result of the crystallization of cristobalite from the silica glass that has previously formed in the clay.

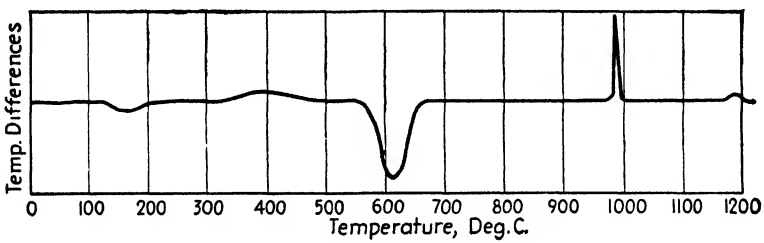

FIG. 100. Thermal curve for a fireclay.

The shrinkage, and conversely the porosity, is a very characteristic property and shows quite clearly the changes that occur in the clay. A typical shrinkage curve for kaolin is shown in Fig. 101. No shrinkage occurs under this slow heating until 450°C (about 840°F) is reached, at which temperature the chemically combined water is driven off, producing a decrease in volume that continues slowly to above 900°C (about 1650°F) where a sharp decrease in volume corresponds to the formation of γ-alumina. At the same time, mullite begins to crystallize. At 1150°C (about 2100°F), glass begins to be formed in larger quantities, which tends to pull the clay grains together, and the shrinkage continues rapidly up to the fusion point of the clay, provided bloating does not occur.

One of the most powerful tools used in studying the changes occurring in a clay is the X ray,[25,28] which gives us an insight into the atomic arrangements of the clay crystals and the altered products. Briefly, however, the recent results of X-ray analysis indicate that kaolinite is unchanged until the chemically combined water is driven off at 450°C (840°F). Above this temperature, there is a noncrystalline structure called "metakaolin" about which we know very little. At 980°C (about 1800°F), the γ-alumina

crystallizes; and immediately afterward, mullite crystals can be detected[15,19,28] even though they are very much finer than would be visible in the microscope. Recent work of Comefpro[37a] and his coworkers indicates that mullite may form directly from the metakaolin without the intermediate γ-alumina.

The microscope does not tell us a great deal concerning the changes occurring in the clay because they take place on such a small scale that an observation of the larger grains shows little. Until the temperature is high enough for large-sized needles of mullite to crystallize out, the microscope is of little help. However, the recently developed electron microscope allows

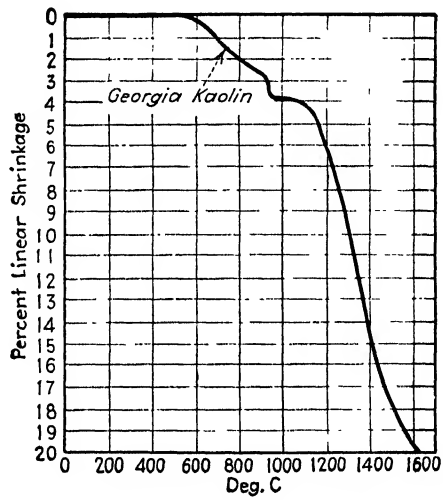

FIG. 101. The shrinkage characteristics of a Georgia kaolin.

us to observe the clay particles at a magnification of as high as 25,000 $\times$, whereby clay particles as small as 0.1 μ can be readily seen. Recently, a very interesting study with the electron microscope by Eitel, Müller, and Radczewski[31] has been made of the breakup of kaolinite on heating to various temperatures. This is the first time that we have had direct visual proof of the reactions going on in the clay. The photographs in this paper are remarkably clear even at the very high magnification and indicate the following reactions: The original clay shows definite hexagonal plates of varying size with clear-cut edges, as reproduced in Fig. 3 of Chap. IV. On heating to 500°C (about 930°F), which is sufficient to drive off the chemically combined water, the only change noted is a slight softening of the edges of the plates. At 800°C (about 1470°F), the plates show slight rounding of the corners and apparently some fine-grained material is thrown off from the edges. Whether this occurred directly in the heating or by

mechanical abrasion of the now soft and friable plate is not certain. At 1000°C (about 1830°F), pseudomorphs of the original kaolinite crystals are still seen, but there is a lack of distinctness with no new crystals in evidence. At 1200°C (about 2190°F), the ground mass of the original kaolinite crystals is filled with small mullite crystals imbedded in glass. More recent work[37a] shows these changes even more clearly.

Another characteristic change in clay on heating is the increase in hardness and mechanical strength after cooling. The raw clay, in many cases, has considerable mechanical strength; but as it is heated to drive off the adsorbed water, this strength usually decreases slightly because of the lessened attraction between the particles. When the chemically combined water is driven from the clay, there is often a further decrease in strength, due to the crystalline breakup; but at 1000°C (about 1830°F) in a pure clay, the strength begins to increase owing to the formation of glass and recrystallization of the remaining components. The strength increases rapidly up to the softening point. In less pure clays, the increase in strength occurs at lower temperatures owing to the earlier glass formation.

Other changes to be noted are variations in color, solubility in acid, and fluorescence of certain dyes in contact with the clay. The last is illustrated by the dye morin, which fluoresces under ultraviolet light when in contact with the alumina group. When clay samples fired to different temperatures are examined in this way, fluorescence will be absent up to 450°C (about 840°F) but will show strongly up to 980°C (about 1800°F) and then less strongly. This indicates the presence of the alumina molecule in the metakaolin.

Picture of the Heat Changes in a Pure Kaolin. In summing up the evidence obtained from the preceding observations of the various changes in the physical properties of a clay, one may start in with a drying temperature of 100°C (212°F). At this temperature, a considerable amount of adsorbed water still adheres to particles, and the finer the clay the larger amount of this water. It is not driven off at any one temperature, but over a considerable range; the more firmly attached water molecules are held until the higher temperatures. This adsorbed water can be removed at low temperatures by confining in an atmosphere free from water vapor, but a considerable amount of time is required. At a temperature of 450°C (about 840°F), the chemically combined water or, more correctly speaking, the OH groups are removed from the kaolinite molecule. It has been shown that with very careful temperature control and long time of heating, this water is driven off very completely at a single temperature, as indicated by the weight-loss curve in Fig. 99, which was taken under carefully controlled conditions. However, even under this condition, there is a small amount of remaining water that is not driven off until 700 or 800°C

(about 1290 or 1470°F) is reached. It is a little difficult to understand just what part of the lattice is occupied by these OH groups which are so firmly held. More probably the gradual weight loss is due to adsorbed water molecules both below and above the crystalline breakup temperature. The condition of the crystal structure between the temperature of removal of the OH groups and the crystallization of alumina has received a great

FIG. 102. Thin section of fused kaolin. This microphotograph shows large mullite crystals embedded in silica glass. The nearly square cross section of these crystals can be seen; 750 diameters with crossed Nicol prisms and gypsum plate.

deal of consideration by various authorities; but at the present time, we seem to have no really definite pictures except that there is a noncrystalline arrangement of the atoms. On the other hand, the structure cannot be entirely broken up, as it is possible to replace the water by comparatively simple hydrothermal action, provided the clay has not been heated above 980°C (about 1800°F) and the subsequent mullite crystals are oriented in relation to the original kaolinite structure. Also the evidence of fluorescence indicates that a sort of alumina molecule is still in existence up to this temperature.

At approximately 980°C (about 1800°F), in the case of kaolin, there is a sudden heat evolution, which is believed to indicate the crystallization of the alumina into the γ-form or the direct formation of mullite. It is interesting to note that the heat effect is greatest for a silica-alumina ratio of 2:1 as it occurs in kaolinite. It is shown by Insley[28] that if the alumina is higher or lower than this particular ratio, the heat effect occurs over a wider range of temperature and is not nearly so marked. He believes that the silica acts in such a way as to stabilize the amorphous structure and prevent crystallization until a certain temperature is reached. This again would indicate that the structure, after the water is driven off, is not entirely random but must have some arrangement by which the alumina crystallization is influenced by the silica.

Immediately after the formation of the γ-alumina, it apparently starts dissolving in the glass and mullite begins to crystallize out. At first these crystals are so small that they can be detected only by the X rays; but at a somewhat higher temperature, they become large enough to see easily under the microscope (Fig. 102).

The heat evolution at 1200°C (about 2190°F) is believed to be due to crystallization of cristobalite from the glass.[28] Such crystals have been detected by Insley, and this seems to be a reasonable explanation. No work has been done to determine this crystallization with less pure clays. Possibly the fluxing effect of such materials as iron oxide and lime might greatly influence it.

TABLE 28. BREAKDOWN TEMPERATURES OF CLAY IMPURITIES

	°C.	°F.
$FeS_2 + O_2 \rightarrow FeS + SO_2$	350–450	660–840
$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2$	500–800	930–1470
$Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$	560–775	1040–1430
$C + O_2 \rightarrow CO_2$	350 →	660 →
$S + O_2 \rightarrow SO_2$	250–920	480–1690
$CaCO_3 \rightarrow CaO + CO_2$	600–1050	1110–1920
$MgCO_3 \rightarrow MgO + CO_2$	400–900	750–1650
$FeCO_3 + 3O_2 \rightarrow 2Fe_2O_3 + 4CO_2$	800 →	1470 →
$CaSO_4 \rightarrow CaO + SO_3$	1250–1300	2280–2370

Effect of Heat on Clay Impurities. Most of the fireclays contain impurities in the form of sulfides and carbonates and also carbon in the form of lignite or bitumen. As the clay is heated in an oxidizing atmosphere, a great many reactions can take place with the eventual loss of the carbon and sulfur by oxidation. There is no opportunity here to discuss these reactions completely, as they are of much more importance to the manu-

facturers of heavy clay products than to the manufacturers of refractories. However, Table 28 will give the more important reactions and the temperatures at which they occur. The upper limit of the temperature is not a very definite one, as it depends on the amount of excess air in the combustion gases, the permeability of the clay, and the size of the object being fired, as well as the interaction between the various impurities. For example, if the pores of the clay contain CO_2 from oxidation of carbon, the increased partial pressure of this gas will delay the dissociation of a material like

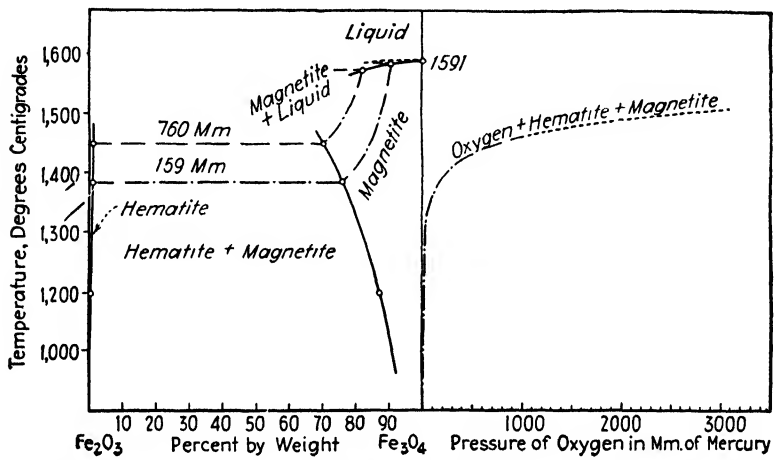

FIG. 103. Equilibrium diagram. The diagram on the left indicates the points that have been determined on the field boundaries by circles or by arrows. The points fixing the isobars are not shown here.

The right-hand diagram gives a curve representing the relationship between the temperature and the pressure of oxygen with which magnetite + hematite can coexist in stable equilibrium. At the lower pressures it represents quite closely the true conditions. In the upper pressure region, however, it can be considered only as giving the order of magnitude of the pressure. (*Greig, Posnjak, Merwin, Sosman, Am. J. Sci.*)

calcium carbonate. In all firing of clays containing considerable amounts of carbon or sulfur, the initial part of the firing process must be carried out sufficiently slowly to oxidize these products completely before the surface pores of the clay are closed; otherwise the well-known black coring will occur.

The system of Fe_2O_3-Fe_3O_4-O_2 is shown in Fig. 103. As the temperature is increased, a higher concentration of oxygen is required to hold the same ratio of Fe to O.

Effect of Heat on Other Hydrated Minerals. The investigation of the relations between the structures, properties, and crystallographic orientations of minerals with the OH ions and their corresponding oxides is very interesting, but to date only meager information is available.

The crystalline breakup by heat of montmorillonite and illite has been studied by Grim and Bradley.[35] Montmorillonite shows a lattice breakdown starting at 600°C (about 1110°F) and complete at 800°C (about 1470°F). A spinel phase appears at 850°C (about 1560°F), but is all dissolved at 1300°C (about 2370°F). Mullite appears at 1050°C (about 1920°F) and increases with increasing temperatures. Illite goes through the same kind of breakup, but mullite does not appear until 1100°C (about 2010°F).

Gibbsite, $Al(OH)_3$, a common constituent of high-alumina clays, has a layer lattice structure in which the Al atoms lie between six OH ions and the layers are packed in such a way that each OH of one layer is opposite an OH of the next layer. At temperatures as low as 150°C (about 300°F), gibbsite loses some of the OH groups and boehmite AlO(OH) is formed, which on further heating above 275°C (about 527°F) forms γ-Al_2O_3,[23] a kind of alumina with a spinel-like structure. A parallelism has been found between the crystallographic orientations of the original and the final crystals as in the case of kaolinite.

On the other hand, diaspore, which is also a common constituent of the high-alumina clays, is more stable than gibbsite and does not lose OH groups until a temperature of 350°C (about 660°F) is reached. The reason for this is evident from its crystal structure; X-ray studies show that its formula should be written $HAlO_2$, and we must think of the H as a small cation in the structure in twofold coordination between a pair of oxygens. Both boehmite and diaspore are dimorphous. On dehydration of diaspore, γ-alumina is formed and, at 550°C (about 1020°F), starts to transform to corundum. The latter transformation is completed at 950°C (about 1740°F), and again there is a parallelism between the orientation of the original and the final crystals. This parallelism in crystallographic orientation illustrates the important role played by the crystal structure in the treatment of raw materials.

It is interesting to note that in a similar fashion, goethite, $HFeO_2$, dehydrates to hematite, Fe_2O_3, and brucite, $Mg(OH)_2$, forms periclase, MgO; in both cases, the original and final crystals are in parallel aggregates. Lepidocrocite, FeO(OH), transforms to γ-Fe_2O_3, which is magnetic and has a spinel-like structure.

At high temperatures, the oxides remaining from the low-temperature reactions, such as iron oxide, lime, and alkalies, react with the clay and form a glass that has a marked influence on the mechanical properties of the finished piece. The oxides also act to a certain extent as catalyzers or mineralizers to increase the rate of growth of the mullite crystals and thereby influence the finished products. It is highly desirable to produce in the clay body a sufficient amount of glass to allow recrystallization to

take place and act as a bonding agent to give good mechanical strength. The lower the temperature at which this can take place the less expensive will be the burning operation. On the other hand, it is undesirable to have too much or too fluid a glass in the finished refractory; in which case, it will show deformation at temperatures so low that its use will be limited. For example, refractories made from pure kaolin must be fired at comparatively high temperatures in order to complete the firing shrinkage and produce sufficient mechanical strength; but when so fired, they give excellent refractory properties. Less pure fireclays can be initially fired at much lower temperatures owing to the more abundant formation of glass, but this glass limits their upper temperature of use.

Firing Shrinkage and Porosity of Clays. When studying a new clay, one of the most instructive tests is the determination of the shrinkage and porosity when fired at different temperatures. This information enables the prediction of the usefulness of the clay when used in a refractory for any particular purpose.

The methods used for measuring shrinkage are comparatively simple. A series of specimens carefully formed may be fired at a number of temperatures, and a decrease in volume or a linear dimension determined for each one. Also a continuous shrinkage curve for a clay can be made by increasing the temperature at a steady rate and measuring the length of the specimen as described for shrinkage measurements in Chap. XVII. It should be noted that these values include the reversible expansion. As will be explained later, to obtain consistent shrinkage measurements, the original specimens must be formed under exactly the same conditions of water content and pressure.

The porosity of the fired specimen is due to both closed pores and open pores. The usual method of determining porosity, which we call "apparent porosity" because it does not include the closed pores, may be determined by filling the pores with water or air, as described below.

The apparent porosity of a small sample is usually measured by making three weighings: the first, the dry specimen; the second, the saturated specimen immersed in water; and the third, the saturated specimen suspended in air.[52] It is quite necessary to be sure that the specimen is thoroughly saturated; and in order to do this, it should be boiled in water for 2 hr. Even with this precaution, there will be some closed pores that the water cannot reach; consequently this method generally gives a low value for the porosity. The porosity is determined from these three weighings by the following formula:

$$P = \frac{W - D}{W - A} \times 100$$

where P = the percentage porosity
W = the weight of saturated specimen in air
D = the weight of dry specimen in air
A = the weight of saturated specimen in water

The volume can be directly measured by a mercury volumeter to give a higher precision. The instrument described by Goodner[38] is convenient for this purpose.

When the porosity of the full-sized brick is to be obtained, it will be found that the previous method cannot always be used because the water

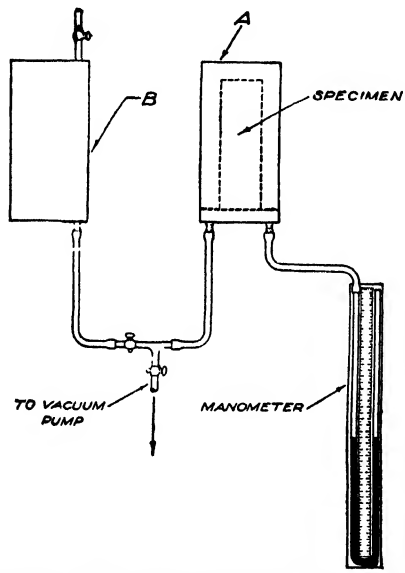

FIG. 104. Apparatus for obtaining the porosity of a brick by the vacuum method.

will run out of the pores when the weighing W is made. The porosity is best obtained in this case by a vacuum method, the principle of which is shown in Fig. 104. A brick is placed in chamber A and sealed tight. The chamber B is empty but of known volume. Chamber A is then connected to a vacuum pump and pumped down to a vacuum of about 700 mm. The connection to the pump is then closed; the connecting cock between the two chambers is opened; and the change in reading of the manometer is noted. The porosity of the brick is then calculated by the following formula, using the constants of the apparatus.

$$S = V_b \frac{P_2}{P_1 - P_2} - (V_a - V)$$

where S = the pore volume
V = the volume of specimen (bulk)
V_a = the volume of chamber A
V_b = the volume of chamber B
P_2 = the equilibrium manometer reading
P_1 = the evacuated manometer reading

The precision of the instrument can be checked at any time by measuring the porosity of a block of iron or any other nonporous material, which should, of course, work out to be zero. This method is rapid and reasonably precise, as air can find its way into smaller pores than can water.

It will be noted in the formula given above that the bulk volume of the brick is required. In some cases where the brick is even and smooth in size,

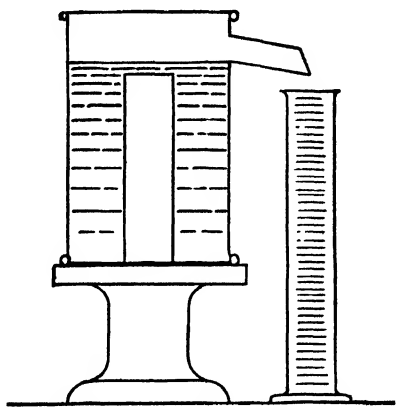

FIG. 105. An overflow can for measuring the volume of a brick.

the volume can be determined by linear measurements, but usually it is better to obtain the volume directly, which is most readily accomplished by saturating the brick with melted paraffin. The surplus is carefully wiped off, the brick is then immersed in an overflow can, as shown in Fig. 105, and the displaced water weighed or measured.

The volume can also be obtained by immersion in mercury[46] or sand. The former method is accurate but requires considerable clean mercury, which is not always convenient. The latter method is simple but not very precise unless great skill is used in packing the sand to exactly the same extent each time.

The determination of the closed pores is best carried out by grinding the specimen fine enough to break into all the pore spaces and then measuring the true density of the powder by the well-known picnometer method (Chap. XX). From the values of true density d_t and bulk density d_b of

the original specimen, the true porosity, *i.e.*, the total volume of the closed and open pores in relation to the bulk volume, can be determined by the following formula:

$$p = \frac{d_t - d_b}{}$$

Table 29 shows the relative amount of closed and open pores in some refractories.[40]

TABLE 29. PRECISION OF POROSITY DETERMINATIONS

Material	Average specific gravity	Average true porosity	Error due to closed pores by water method	Error due to closed pores by vacuum-method
Silica brick	2.31 to 2.33	27.2 to 28.3	0.3 to 1.9	−0.15 to −0.18
Magnesite brick	3.54 to 3.56	25.6 to 29.5	0.3 to 1.1	0.0 to 0.3
Flint-clay firebrick	2.67 to 2.72	27.7 to 32.6	3.7 to 10.2	1.5 to 7.0
Plastic-clay firebrick	2.66 to 2.69	15.9 to 22.8	1.0 to 4.0	0.0 to 0.3

The firing shrinkage and porosity are influenced quite markedly by the conditions under which the specimen is molded. Obviously, the more densely the raw clay is packed the less will be the firing shrinkage when carried to a given final porosity. Therefore, high pressure in molding, proper water content, and the fineness of the clay all influence the amount of shrinkage.

Figures 106 to 110 show curves of shrinkage and porosity values for a number of typical fireclays. These illustrations give a general picture of

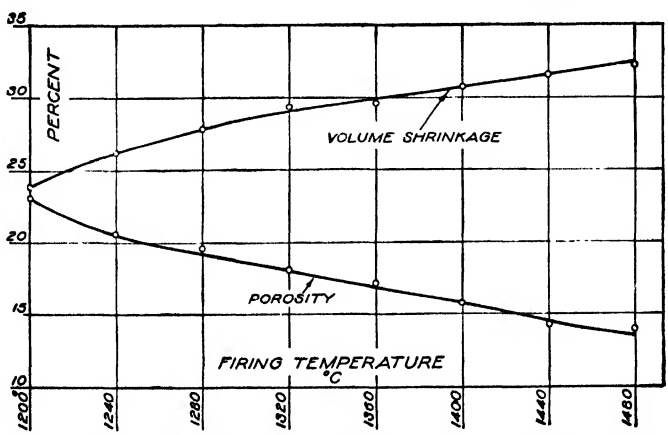

FIG. 106. Raw smooth flint clay, Missouri. (*J. Am. Ceram. Soc.*)

the shrinkage and porosity values of the clays; but for any particular problem, firing tests should be made under the exact conditions to which the clay will be subjected.[57] In Table 30 are given average porosity values for some typical refractories.

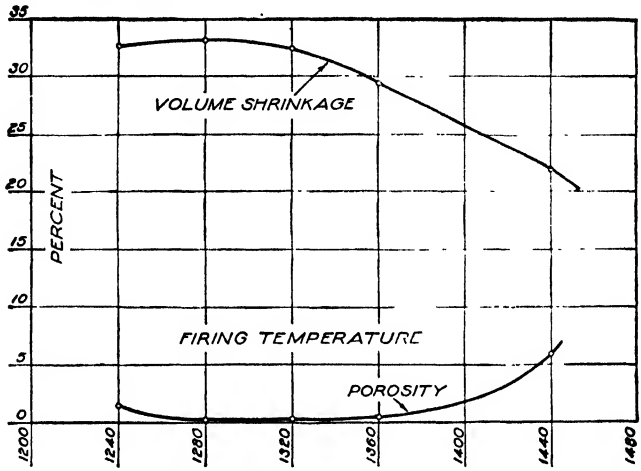

FIG. 107. Raw plastic clay, Missouri. (*J. Am. Ceram. Soc.*)

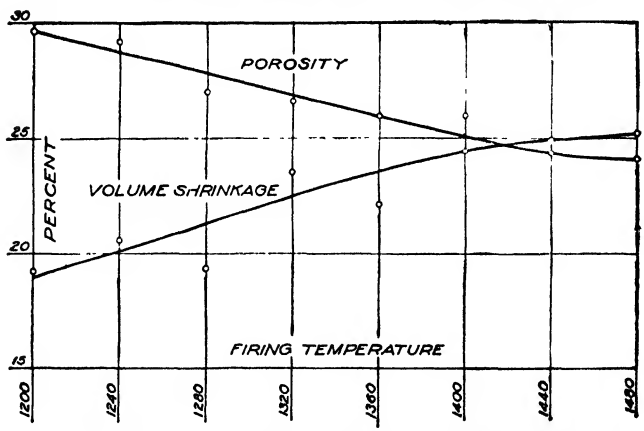

FIG. 108. Raw burley flint clay, Missouri. (*J. Am. Ceram. Soc.*)

It should always be kept in mind that most ceramic bodies never reach equilibrium in firing. Therefore, the firing schedule, or time held at temperature, is as important to control as the temperature level. It has been found[1,21] that decreasing the temperature by about 30°C is equivalent to increasing the time by tenfold.

2. Firing Properties of Nonclay Refractory Materials. *Silica.* Silica, one of the most important of refractory minerals, has received a great deal

of study, and consequently more data on its properties are available than on any other mineral. The most complete treatise on silica is that of Sosman,[75] which the reader should consult for many of the details for which space is not available here.

In nature, silica is very common and most often occurs as the mineral quartz. It is found in many different types of mineral deposits, is an essen-

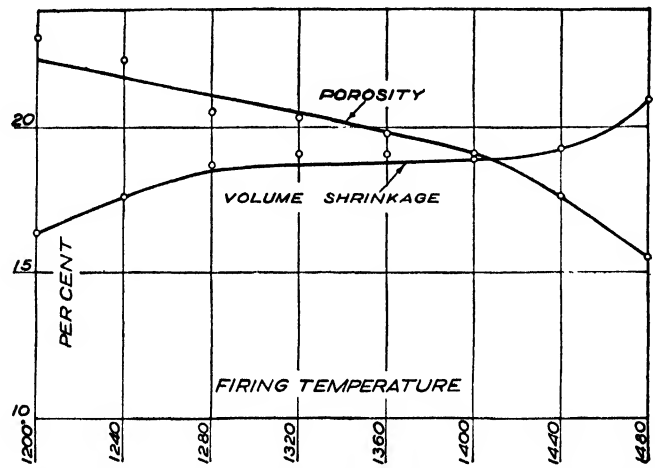

FIG. 109. Plastic bond clay, Cambria County, Pa. (*J. Am. Ceram. Soc.*)

TABLE 30. POROSITY OF REFRACTORIES

Type of Brick	Average Porosity, Per Cent
Hand-molded fireclay	24
Stiff-mud fireclay	21
Dry-pressed fireclay	22
Kaolin	18
High alumina, 70 per cent	32
Magnesite	23
Magnesite, chemical bond	11
Silica	25
Forsterite	25
Chrome-magnesite	25
Chrome	23
Chrome, chemical bond	11
Tank blocks: Flux	20
Grog	7
Fused	0
Silicon carbide, clay bond	20
Insulating firebrick: 2.5 lb	75
1 lb	90

tial constituent of such acid igneous rocks as granite and rhyolite, and also occurs in veins, in sedimentary rocks such as sandstones and quartzites, and in unconsolidated river and beach sands.

Quartz can be transformed by heating into a number of polymorphous modifications. These forms, together with their stability ranges, are shown in Fig. 111 taken from Sosman.

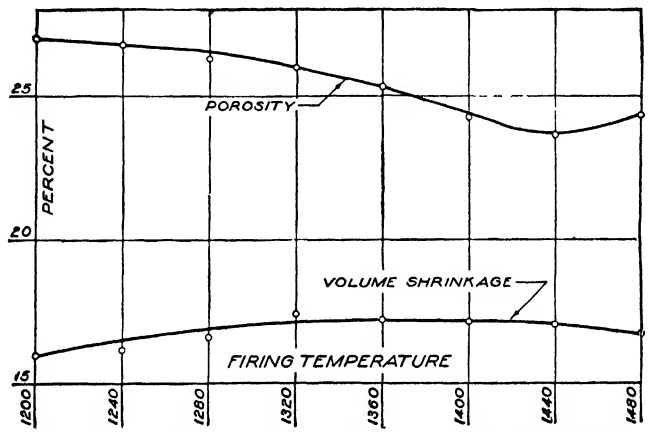

FIG. 110. Dean flint clay, Pennsylvania. (*J. Am. Ceram. Soc.*)

There are at least six crystalline varieties of silica: quartz, tridymite, and cristobalite and each of these has a high- and a low-temperature modification. All the varieties are characterized by a three-dimensional network of SiO_4 tetrahedrons, each corner being shared with neighboring tetrahedrons. Thus a silicon atom is always shared by two oxygens, which checks the formula SiO_2, long ago determined by chemical analysis.

Figure 112 shows models that illustrate the manner in which the atoms are arranged in high- and low-temperature cristobalite, high-temperature tridymite, and high- and low-temperature quartz. The silicon atoms nestle in the center of four oxygen atoms and are not visible in this picture. The

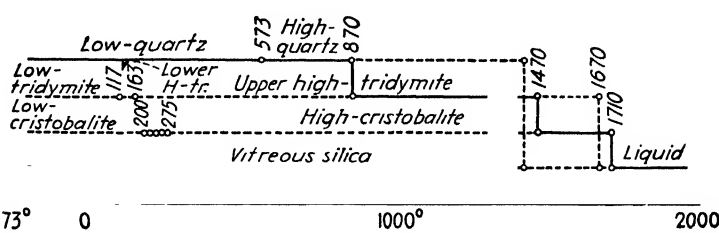

FIG. 111. Polymorphous modifications of silica and their stability ranges. (R. B. Sosman, "The Properties of Silica," *New York, Chemical Catalog Company, Inc.; Reinhold Publishing Corporation*, 1927.)

models are not arranged in a similar crystallographic orientation but rather to show the major features of each structure. One immediately apparent feature is that cristobalite and tridymite are more open packed and have large holes whereas the atoms in high- and low-temperature quartz are

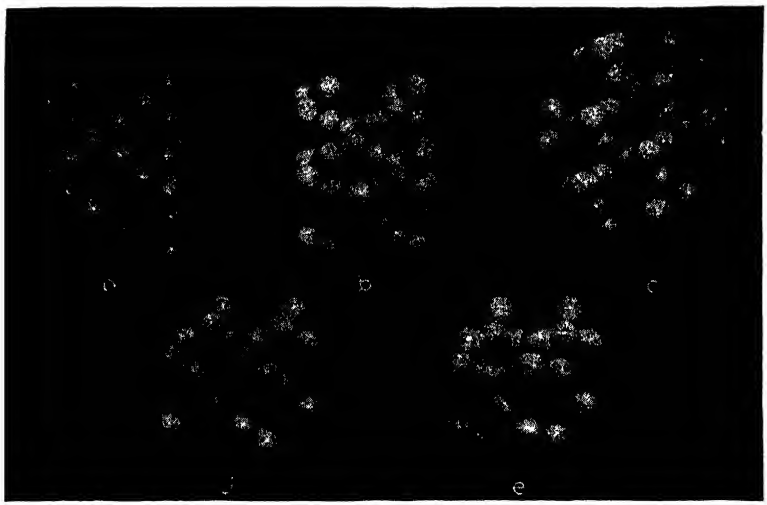

FIG. 112. Models showing the arrangement of atoms in various polymorphic modifications of silica, SiO_2. (*a*) High cristobalite, (*b*) low cristobalite, (*c*) high tridymite, (*d*) high quartz, (*e*) low quartz. The silicon atoms are not visible because they are small and nestle in a tetrahedron formed by four oxygen atoms. The models do not have similar crystallographic orientations. Note that the low-temperature forms are more closely packed than the high-temperature forms.

tightly packed together and form a close-packed structure free from large holes. Hence, the density and refractive indices of tridymite and cristobalite are very similar, but they differ considerably from those of quartz, as is shown in Table 31.

TABLE 31. DENSITY OF FORMS OF SILICA
At Room Temperature

	Index of refraction*	Density†	Density‡
Quartz	$\epsilon = 1.553$, $\omega = 1.544$	2.65	2.653–2.660
Tridymite	$\alpha = 1.469$, $\beta = 1.473$, $\sigma = 1.470$	2.26	2.28–2.33
Cristobalite	1.486	2.32	2.27

* Larsen and Berman.[89]
† Rogers.[95]
‡ Dana.[97]

Quartz is remarkably pure, and consequently the values for its indices of refraction and density are usually very closely alike. There are only meager data on the chemistry of tridymite and cristobalite, but the data that are available indicate that they are usually impure and consequently vary in density and refractive index. On the other hand, it is quite possible that these variations may be due to the little care usually given to the selection of material for such measurements.

In all cases, the high-temperature forms have a higher symmetry than the low-temperature forms. Note that the diagonal groups of tetrahedrons in high-temperature cristobalite form nearly a straight line whereas in low-temperature cristobalite, they form a puckered chain; the same is true in the high- and low-temperature-quartz relationship, although the effect is less apparent in the picture. The differences between the linking of the tetrahedrons in the high- and in the low-temperature forms of each mineral are slight, but they are considerable in quartz, tridymite, and cristobalite. When a high-temperature form is transformed to a low-temperature form, the tetrahedrons are shifted and rotated but none of the links is broken, and consequently the high-low transformations of each mineral are rapid and reversible (see Fig. 111). These inversions are accompanied by volume changes, given in Table 32 below, together with the heat effects that produce them.

TABLE 32. DENSITY CHANGES ACCOMPANYING INVERSIONS

Form	Density change	Heat effect, g. cal. per g.
Quartz, low-high	−0.02	4.5
Cristobalite, low-high	−0.04	5.0
Tridymite, low-lower high	−0.01	1.0
Tridymite, lower high-high	0.00	

The structures of the minerals quartz, tridymite, and cristobalite are quite different from one another, and the transformation of one to the other requires a marked change in the linking of the tetrahedrons. Consequently these transformations are extremely slow, and tridymite and cristobalite can exist indefinitely in the metastable state at room temperature. In fact, it is impossible to form quartz from either tridymite or cristobalite by strictly thermal reactions.

The sluggish inversions that are so important to the manufacturers of silica refractories can be greatly influenced by other materials called "mineralizers." A great deal of work has been done on the effect of mineralizers in changing quartz to cristobalite or tridymite in the kiln, and

many of these are noted in the references at the end of the chapter.[68,69,70,72,81,82,83,84,97,99] The most common one is lime, which is used in most of the commercial silica bricks, partly as a bond and partly as a mineralizer, to hasten the conversion of the quartz to cristobalite and tridymite (Fig. 113). Many other mineralizers have been suggested, such as fluorides, titanium dioxide, boric oxide, ferric chloride,[85] and sodium chloride. It should be

FIG. 113. Thin section of silica refractory showing a typical wedge-shaped twin crystal of tridymite. There are several less distinct crystals in the field. The surrounding material is cristobalite; 750 diameters, with crossed Nicol prisms and gypsum plate.

remembered, however, that in commercial production, it is undesirable to cause the inversion to proceed with too great rapidity; for if the volume change proceeds too fast, it will rupture or make unsound the structure of the brick.

Kyanite and Associated Minerals. Kyanite (triclinic), andalusite (orthorhombic), and sillimanite (orthorhombic) all have the formula Al_2SiO_5. The structural relations of these minerals are complex, and for a general discussion the reader should see Bragg.[110] On heating, they change over to mullite and glass or to mullite, glass, and cristobalite. The crystal-

line breakup of these minerals has been thoroughly studied by Greig,[104] and the temperature ranges are shown in Table 33.

TABLE 33. DECOMPOSITION TEMPERATURES OF SILICA-ALUMINA MINERALS

Mineral	Kyanite	Andalusite	Sillimanite
Decomposition starts	1100°C. (2010°F.)	1410°C. (2570°F.)	1550°C. (2820°F.)
Complete decomposition*	1410°C. (2570°F.)	1500°C. (2730°F.)	1625°C. (2960°F.)
Peak on thermal curve	1420°C. (2590°F.)	1510°C. (2750°F.)	1560°C. (2840°F.)
Density before firing	3.6–3.7	3.1–3.3	3.3

* This temperature varies with rate of heating and size of grains.

As the density of the mullite is 3.16 and the density of the silica glass and cristobalite is less, it is obvious that there must be an expansion in volume during the conversion. This expansion is particularly evident in the case of kyanite, which has the highest original density, but shows only to a very small extent with the other two minerals. The expansion of kyanite on heating[106,111,112] may be a valuable property when combined with clays, as it offsets the shrinkage of the clay. Unfortunately, however, the expansion of the kyanite takes place through a rather small temperature interval, whereas the shrinkage of the clay continues over a much longer range; consequently the two effects do not exactly balance each other. As will be shown later, however, a refractory can be produced that will have exactly the same fired volume as the initial volume. The expansion characteristics of kyanite are greatly dependent on the size of the grains, a fact that should be taken into account when considering the total expansion.

The difficulty in getting kyanite during the last war has led companies in this country and Germany to produce mullite type brick from other materials. The general method seems to be the calcination of bauxite and clay[291] in a rotary kiln to form grog and then bond this together with raw material and fire to high temperatures.

Topaz. Topaz, $Al_2SiO_4(F,OH)_2$, which has recently been found in some quantity in South Carolina, contains enough alumina to form largely mullite on firing.[113] The fluorine accelerates the reaction but is eventually completely driven off together with the water.[114]

Magnesite. The firing properties of magnesite depend largely on its composition. For refractory purposes, a dense, low-porosity material is desired. On heating the raw magnesite, the CO_2 is driven off at temperatures between 400 and 900°C (about 750 and 1650°F), forming immediately the only known form of MgO, periclase. At first these crystals

are so minute that they can be detected only by means of X rays; but with increasing time and temperature, they grow until they form the usual honeycomb structure shown in Fig. 114. It should be remembered, however, that the periclase crystal is cubic and not hexagonal.

The burned magnesite has a true density of 3.55 to 3.63 and a porosity of 15 to 27 per cent. The greater the impurities present and the higher

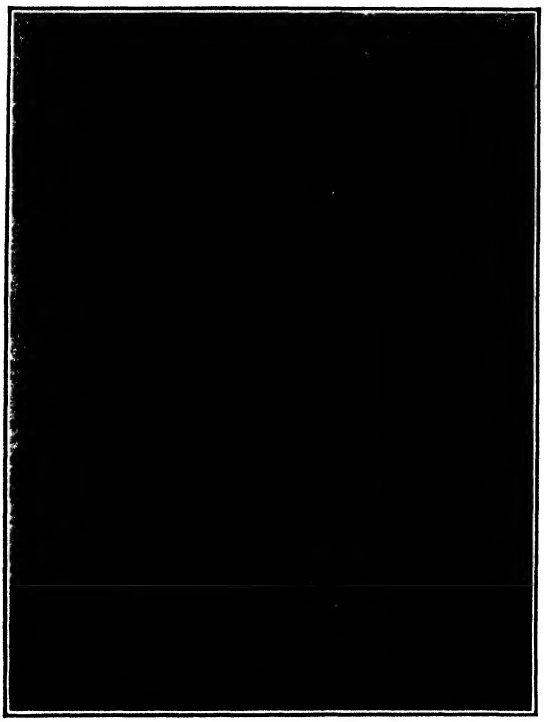

FIG. 114. Thin section of Grecian magnesite burned at 1790°C (3250°F), which shows the rather typical honeycomb structure of calcined magnesite, and, in addition, small birefringence areas between the boundaries of the small grains. The latter is due to small amount of impurities reacting with the magnesite at high temperatures; 60 diameters, with crossed Nicol prisms and gypsum plate.

the firing temperature the lower the porosity. It is desirable to fire the grain well so that no appreciable shrinkage will occur on firing the brick.

The bond in magnesite refractories is mainly glass, but crystalline material such as forsterite does occur. Iron oxide, in the form of finely divided magnesioferrite, $MgFe_2O_4$, occurs to the extent of 7 or 8 per cent in some types of magnesite, which allows the production of a strong and dense product at temperatures very much lower than would be possible with the pure magnesia. Other impurities such as lime, silica, and alumina

form glass, which acts as a bond. The burning process is discussed in the references.[118,119,123,124]

Lime. Calcium carbonate can be decomposed readily to calcium oxide; and on heating at temperatures as low as 1400°C (about 2550°F), crystals of calcium oxide can be formed. Such crystals are chemically much more stable than the low-calcined lime and undoubtedly would serve as an excellent basic refractory if they could be properly protected from moisture.

Zirconia. There are a number of polymorphous modifications of zirconium dioxide, and for a general review the reader should see the papers by Ruff and Ebert,[137] Cohn,[142] and Clark and Reynolds.[143] The natural mineral baddeleyite is monoclinic. Pure monoclinic ZrO_2, often called the "*C* form," is stable up to 1000°C (about 1830°F) where it is transformed to the β form, which is tetragonal; this transformation is reversible. The tetragonal form is transformed irreversibly at 1900°C (about 3450°F) to the α_2 form, which is trigonal. The α_2 form is transformed to the α_1 form, which is also trigonal, at 625°C (about 1160°F), an inversion that is rapid and reversible.

It should be remembered that the inversion temperature and the crystallographic modifications obtained at various temperatures are dependent to a large extent on the composition and impurities that are present. This is again true in the ZrO_2 system. If the nitrate, oxychlorate, oxylate, or certain hydroxides of zirconium are heated, the tetragonal form is obtained at temperatures around 600°C (about 1110°F). This tetragonal form is metastable and is converted to the monoclinic form on further heating. The tetragonal form is also obtained if pure zirconia is heated in the presence of silica at about the same temperature; but whereas the tetragonal form obtained by heating the above-mentioned compounds of zirconium is transformed to the monoclinic form on further heating, the silica-bearing form remains tetragonal up to 1460°C (about 2660°F), where it is transformed to zircon, $ZrSiO_4$. If certain oxides such as MgO and CaO are present, a cubic form is obtained at about 1700°C (about 3090°F). This isometric form does not transform on cooling and is obtained only in the presence of the oxide impurities (other types of impurities might act in the same way). Less than 3 per cent magnesia in solid solution will give rise to the isometric form, and the maximum amount of magnesia that exists in solid solution in ZrO_2 is about 28 per cent, which corresponds to the formula $Mg_2Zr_3O_8$.

The most useful compound of zirconium other than the oxide is zirconium silicate, which corresponds to the natural mineral zircon, $ZrSiO_4$. This is a stable mineral and can serve as a useful refractory material.

Chromite. Chromite is the natural spinel-type mineral of theoretical formula $FeCr_2O_4$. It is thermally stable and apparently undergoes no

polymorphous modifications up to the fusion point. However, the natural mineral always contains impurities in solid solution, such as Ca, Mg, and Al, and admixed mineral impurities such as the silicates. Silica, if in large quantity, is objectionable, as it forms considerable quantities of glass on heating, which lowers the mechanical strength of the chromite refractories at high temperatures. The addition of MgO in the right amount to form the compound forsterite will diminish the amount of glass and provide a superior refractory (see the patents of Seil[163]). Considerable study has been given to bricks of mixtures of magnesite and chromite,[152,154,155,158,160] which have given trouble because of a gradual growth due to absorption of iron oxide. Chrome-silica bricks[150,151] and chrome-alumina bricks[153] have been suggested.

Titania. Titanium dioxide also has several modifications and Cohn[142] has suggested the interesting analogy between SiO_2, ZrO_2, and TiO_2 as shown in Table 34.

TABLE 34.

SiO_2	Quartz	Cristobalite	Tridymite
ZrO_2	Baddeleyite	β-Zr_2O_3	α-Zr_2O_3
TiO_2	Brookite	Anatase	Rutile

Magnesium Silicate Minerals. There are a number of minerals of this class such as olivine, talc, and serpentine, which may form the basis of forsterite refractories.[171,172] In most cases, sufficient magnesite must be added to the natural mineral to convert the low-melting metasilicate to the high-melting orthosilicate. The amount of magnesia added as well as the grain size of the various minerals are quite important and are covered by patents such as that of Goldschmidt.[167,168]

Carbon. Blocks made of granular coke and tar are fired in special kilns[291,292] where they can be completely surrounded by finely ground coke to prevent oxidation of the block. The firing takes 2 or 3 weeks with a maximum temperature of 700 to 800°C (about 1290 to 1470°F). The finished blocks have a crushing strength of 3,000 to 10,000 psi and a porosity of 20 to 30 per cent.

3. Solid Reactions. *Importance in Ceramic Processes.* A great many ceramic firing processes take place with little or no liquid phase present; accordingly many believe that the reactions go on entirely between solids. In spite of the great importance of these types of reactions, it was not until recently that a thorough study was made of this phenomenon, although as early as the year 1909, Wright pointed out the fact that calcium oxide

crystals would grow rapidly at least 1000°C (about 1830°F) below their fusion point. Most of the early work in this field has been carried out in Germany by G. Tammann and his coworkers and by Goldschmidt. A very good résumé of the subject is given by Taylor,[197] and some practical aspects of the subject are discussed in Chap. XII.

Mechanism of Solid Reactions. Solid reactions apparently take place because of loosening of the atomic bonds by thermal agitation, which permits mutual diffusion of the various atoms into the adjacent parts of the structure. The solid reactions can be divided logically into two groups; the first in which we simply grow large crystals from small ones and the second group where we produce a new type of crystal from two dissimilar ones.

The process of diffusion is greatly influenced by many factors in addition to the composition of the original crystals. In the first place, it has been found that the solid reaction progresses much more rapidly at a temperature where one of the crystals involved passes through an inversion point.[186] For example, if a solid reaction is going on between quartz and another mineral, the reaction would be greatly accelerated at a temperature of 573°C (about 1060°F) where the low-temperature quartz changes to the high-temperature form. This is probably due to the loosening of the bonds at the inversion point and permitting of much greater rates of diffusion. It has also been found that gases, such as water vapor and fluorine, act as mineralizers and greatly accelerate the solid reaction. Again the reactions proceed much more rapidly, as we should expect, when the reacting particles are fine and in intimate contact. It has also been found that the reaction can be accelerated by seeding the mass of reacting crystals with a few fragments of the new crystal to be formed.

One example of a solid reaction is the production of periclase crystals of considerable size at temperatures far below the softening point. This is the type of reaction where fine crystals are changed into large crystals of the same kind. Another example is the production of spinel from magnesium oxide and alumina. Here an entirely new crystal is formed, and this can be carried out at temperatures far below the point where any liquid could be formed in the system.

The mechanism of sintering of nonglassy refractories is a type of solid reaction, but as yet we know very little about the process. Pure granular particles are pressed together to a porosity of, say, 30 per cent and then fired to 80 or 90 per cent of their melting point. In the firing process the pores disappear and a dense body results. What are the forces that close up these pores? Is it surface tension that closes each pore and forces the enclosed gas into solution in the crystal? Or is it a form of recrystallization where the surface energy causes loss from the small crystals and gain by the

large crystals in the vapor phase? We certainly do not know the answer at present, and fundamental research on this subject is badly needed.

4. Hot Pressing. *Principle.* If a powdered material is heated to a temperature somewhat below its melting point, there is a tendency for the powder to sinter together and gradually approach a nonporous mass. If glass is present, this sintering goes on over a considerable temperature range as with the ordinary refractory or whiteware body; but if there is no glass present, the sintering occurs in a narrower temperature range as discussed in the preceding section on solid reactions. It has been known for a long time that if external pressure is applied to the powder while it is being heated,[242,243] this sintering is greatly accelerated and the particles coalesce into a solid mass at a very much more rapid rate and at a lower temperature level. Little has been published concerning the mechanism of sintering under pressure, and this is a very fruitful field for research. The work of Buerger,[249] Washken,[246] and Shaler[248] should be consulted as about the only published scientific approach to the subject.

Sintering under pressure has certain obvious advantages, such as the production of low-porosity refractory bodies, which would be difficult to form in the usual firing operation. It is also possible to produce articles very accurately shaped, as there is little shrinkage or distortion during the operation. Another advantage is the fact that the operation can be carried out very rapidly, saving considerable time and labor. Again the raw material does not have to be carefully sized, and binders or lubricants are not needed.

On the other hand, there are certain disadvantages, as a temperature cannot generally be used above the point where the powder will react vigorously with the mold. Then again, at the high temperatures the life of the mold is short. Also, means must be provided for slowly cooling the finished piece to prevent cracking if it is a nonmetal.

Methods. One of the simplest methods of hot pressing is to introduce a heated object, or compact, into a cool mold and press it instantly, which might be called a "coining" process. This method can be used for some of the metals and possibly metal carbides; but as far as is known, it has not been used for other refractories. This method has the advantage of using a cool mold, which can be made of steel or tungsten carbide, but it means that the operation must be carried out very rapidly before the mold has time to chill the compact and also the finished piece must be removed from the mold before it has time to heat the walls.

Most of the hot pressing of nonmetals has been done in heated molds, usually of graphite.[242] The heating can best be carried out by either resistance or induction methods. An example of the former is given in the

Ridgeway and Bailey patent[240] illustrated in Fig. 115. The heating cylinder is made of graphite and fitted with two water-cooled electrodes through which the heavy current needed for heating is supplied. The powder to be pressed, in this case boron carbide of 200 mesh, is loaded into the mold as shown. The floating core, mold walls, and plungers are also made of graphite. The load is applied by a lever and weight, although an air cylinder could be used, with pressures up to 5,000 psi and temperatures up to 2350°C (about 4260°F). This furnace can be operated continuously or periodically for production use.

The heating can also be carried out by induction. In the case of a conducting powder, such as a metal, the heat is generated in the charge itself. In most cases, it is necessary to induce the heat in a conducting sleeve, or susceptor, forming the mold wall. A diagrammatic sketch of a suggested apparatus for hot pressing is shown in Fig. 116, where *a* is the powder to be compacted between the plungers, *b*, which are forced together with a hydraulic press. The heat is induced in the graphite susceptor *c*, with a removable graphite liner *d*. The hole *e* is used to measure the temperature with an optical pyrometer. The water-cooled, copper inductor *f* surrounds the quartz tube *g* and is insulated from the susceptor with powdered graphite *h*.

For commercial production, it appears at the present time that graphite is the only material satisfactory for a liner. Therefore, the temperatures are limited to the level at which reaction occurs between the powder and the liner. These reaction temperatures are given in Table 35.

TABLE 35. REACTION TEMPERATURE BETWEEN PURE GRAPHITE AND PURE REFRACTORY MATERIALS*

Refractory	Temperature	
	°C	°F
MgO	1800	3270
BeO	2300	4170
ZrO_2	1800	3270
ThO_2	1950	3540
W	1500	2730
Mo	1600	2910

* From thesis of P.D. Johnson, Massachusetts Institute of Technology, 1948.

If the reaction temperature is below the temperature at which the powder becomes plastic, this method of hot pressing cannot be used, but it is believed that many of the high-temperature materials can be pressed in graphite.

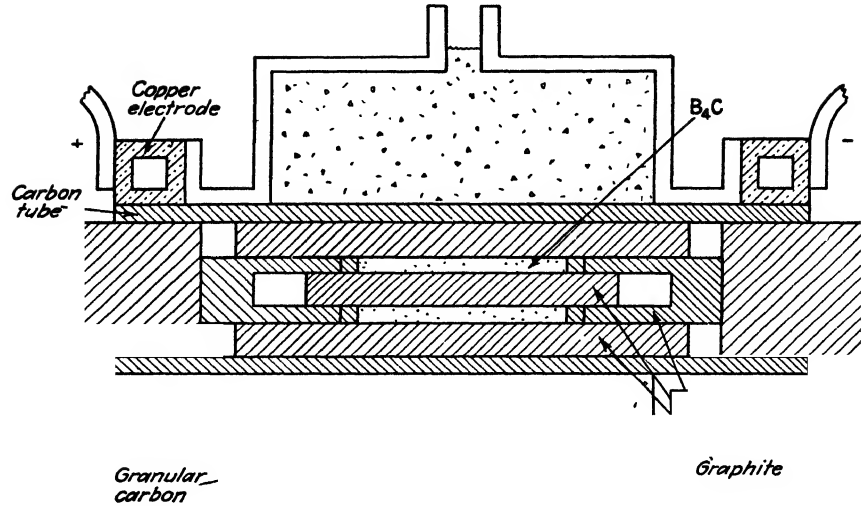

FIG. 115. Ridgeway's method of hot pressing.

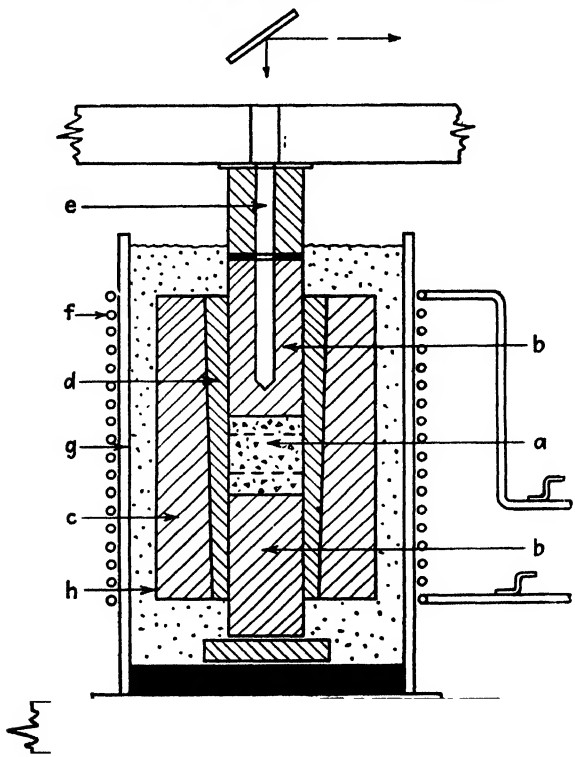

FIG. 116. Induction-heated hot-pressing die.

TABLE 36. PHYSICAL PROPERTIES OF HOT-PRESSED MATERIALS*

Material	Formula	Density (as molded)	Melting point, °C	Porosity, per cent	Hardness (Knoop, 100)	Compressive strength, psi	Transverse rupture, psi	Electrical resistivity microhm per cm	Thermal expansion (20–800°C) $\times 10^{-6}$ per °C	Young's modulus 10^{12}, dynes per sq cm
Oxides:										
Aluminum oxide...	Al_2O_3	3.86–3.99	2035	0–3	2,050	373.000	22,000		7–9	3.7
Beryllium oxide..	BeO	2.85–3.01	2570	0–5	1,250	231,000	24,000		8–9	3.8
Magnesium oxide.	MgO	3.4–3.5	2800	2–5		112,000			14	2.5
Thorium oxide....	ThO_2	9.55	3050	5						
Zirconium oxide (CaO stabilized).	ZrO_2	5.68	2650	6	1,160					2.2
Chrysoberyl.....	$BeO{\cdot}Al_2O_3$	3.6	1870	2						
Spinel.....	$MgO{\cdot}Al_2O_3$	3.5	2100	2	1,270					
Carbides:										
Boron carbide..	B_4C	2.51	ca .2500	0	2,800			3×10^5–8×10^5	4.5	4.5
Beryllium carbide..	Be_2C	2.20		10	2,410			5.6×10^4	12	
Silicon carbide....	SiC	2.8	ca .2600 (decomp.)	13+	2,550			5×10^7–2×10^8		
Tantalum carbide..	TaC	13.66	3800 ± 150	6						6.3
Titanium carbide.	TiC	4.80	3140 ± 90	3	2,470			170		
Vanadium carbide.	VC	5.42	2800	7	2,080			160		
Tungsten carbide..	WC	15.61	2870	0	1,880					5.4
Zirconium carbide.	ZrC	6.27	3530 ± 125	5	2,090			50		3.4
Nitrides:										
Beryllium nitride .	Be_3N_2	2.45		17	2,040					
Titanium nitride..	TiN	5.29	2950 ± 50	3	1,770			72		
Zirconium nitride..	ZrN	6.65	2980 ± 50	6						

* Data in this table furnished by the Norton Co., Worcester, Mass.[350]

Applications. The hot-pressing method has already been used to some extent in powder metallurgy with commercial success for some types of articles, but very little information is available in the literature.[241,242,243]

Nonmetals can be hot pressed quite satisfactorily,[245] and the data in Table 36, kindly supplied by the Norton Company,[250] Worcester, Massachusetts, give the physical properties of a number of high-temperature refractories formed by a hot-pressing operation. These properties indicate great promise for this method of fabrication.

It has been reported that pieces as large as a standard brick have been formed by the hot-pressing operation, and there is considerable interest in developing this process for the larger shapes, such as nonporous tank blocks. But the cost of heating and the short life of the molds at present do not seem to give much promise of making this a method adaptable to large-scale production. However, it would seem desirable to carry out a great deal more development in this field, as means may be found to overcome these difficulties.

5. Firing Properties of Refractory Bodies. It is seldom desirable to produce a refractory directly from a raw plastic clay because of the large shrinkage and distortion that would occur in firing. A reduction in firing shrinkage is a very desirable accomplishment for the following reasons:

1. It permits the production of a fired refractory that will be close to the desired dimensions.
2. It prevents warping of the refractory on firing.
3. It permits a greater weight of finished bricks to be fired in a given kiln.
4. It makes it unnecessary to control the maximum temperature of firing as carefully as when large shrinkages occur.

Use of Grog. One of the simplest methods of reducing the firing shrinkage of a refractory is by introducing a nonplastic material such as grog, an ancient expedient but one that carries a patent history.[220,221,230,232,234,236] As this material has already been fired and has reached a stable volume, it acts somewhat as a skeleton to hold the brick together in a stable form during the firing operation. Figure 117 shows a curve of firing shrinkage and porosity of a mixture of kaolin and grog burned to a temperature of 3000°F (about 1650°C) for 2 hr. The grog was sized for dense packing, bonded with raw Georgia kaolin, and formed in a mold by hand. It is interesting to note that the grog alone has a 3 per cent linear shrinkage when fired at this temperature. Careful microscopic studies of individual pieces of the same grog fired at the particular temperature showed no volume change and no rounding of the corners; but apparently when the grog is formed into a mass of particles in contact, the surface tension or pressure effects are such as to cause rounding of the sharp points and edges sufficient to produce welding and shrinkage.

It is also interesting to note that bond clay can be added up to approximately 25 per cent without any change in the burning shrinkage. As the volume of voids in this grog is approximately 25 per cent of the bulk volume, it will be seen that the bond is simply acting as a filler in the pore spaces and that when it shrinks, it does not affect the volume of the whole piece, since this is governed by the grog. However, when the amount of bond is increased beyond 25 per cent, the total shrinkage begins to increase more and more rapidly until 100 per cent of bond is reached. This is due to the fact that thicker and thicker films of shrinking bond are built up between the grog grains.

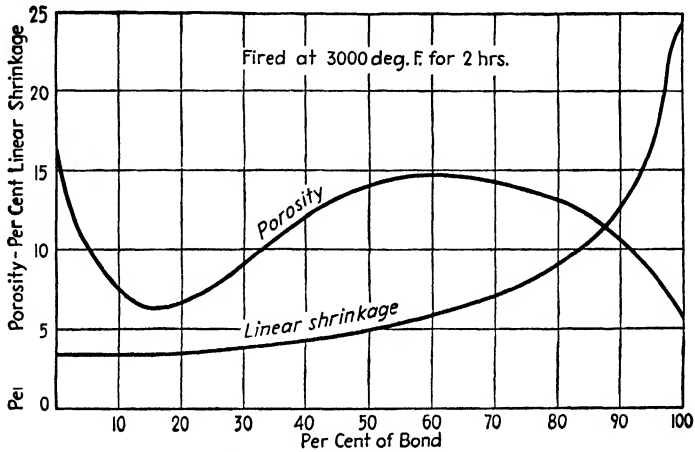

FIG. 117. Shrinkage and porosity curves. Clay-grog mixtures.

Expanding Minerals. The shrinkage of a refractory clay can also be controlled by adding a mineral that expands on firing.[111] Such a mineral may be kyanite, which, mixed with clay in the raw state or with clay and grog, will give a very definite expansion.

To illustrate this, a few mixes were made by Lane[109] using the proportions given in Table 37.

These mixes were molded in a dry press and fired to various temperatures at which they were held for 3 hr. The shrinkage curves are shown in Fig. 118. It will be seen that the kyanite gives a real expansion over the range from 2350 to 2600°F (about 1290 to 1425°C) but beyond this point shrinks faster than the grog and clay mix—a disadvantage when it is attempted to make a refractory to be volume constant at temperatures higher than the original firing. However, the 12 per cent kyanite mixture has the same volume at a firing temperature of 2975°F (about 1635°C) as when molded. Kyanite having too coarse grains ruptures and weakens the structure, whereas too fine grains give little or no expansion. Grains of all

TABLE 37. KYANITE-CLAY MIXES ILLUSTRATED IN FIG. 118

Mix	Dense kaolin grog, per cent	Raw N. C. kyanite, per cent	Raw kaolin, per cent
A	85	0	15
B	81	4	15
C	77	8	15
D	73	12	15

Grog sizing		Kyanite sizing	
Screen	Per cent	Screen	Per cent
4–8	35	14–35	50
8–14	15	35–60	30
14–35	6	60–100	10
35–60	4	100	10
60–100	20		
100	20		

one size break down over a very small temperature range, giving an undesirable peak in the expansion curve.

The minerals sillimanite and andalusite were also tried out in similar mixtures; and although they showed a small amount of expansion, they were not nearly so effective as the kyanite.

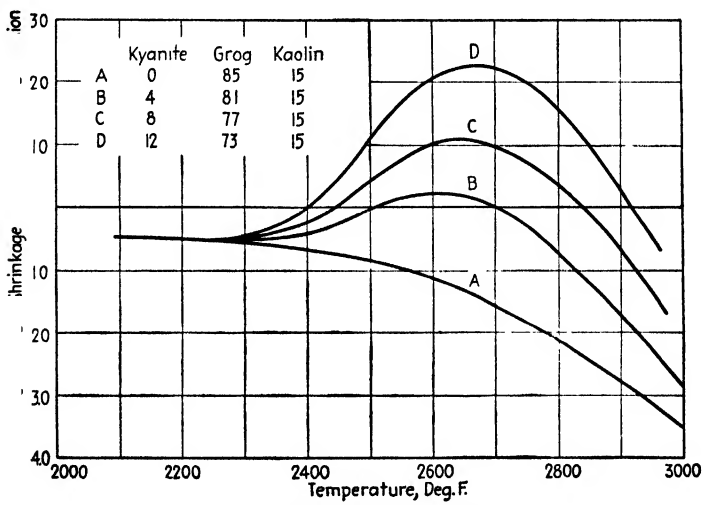

FIG. 118. Expansion caused by kyanite.

It is theoretically possible to add a high-density mineral like fused alumina to a mixture of grog and bond, which after long heat-treatment will dissolve in the glass and form mullite of lower density. Practically, however, this solution goes on with extreme slowness and seems difficult to carry out in a practical way, although such a method is suggested in a patent of Lambie and Ross.[60]

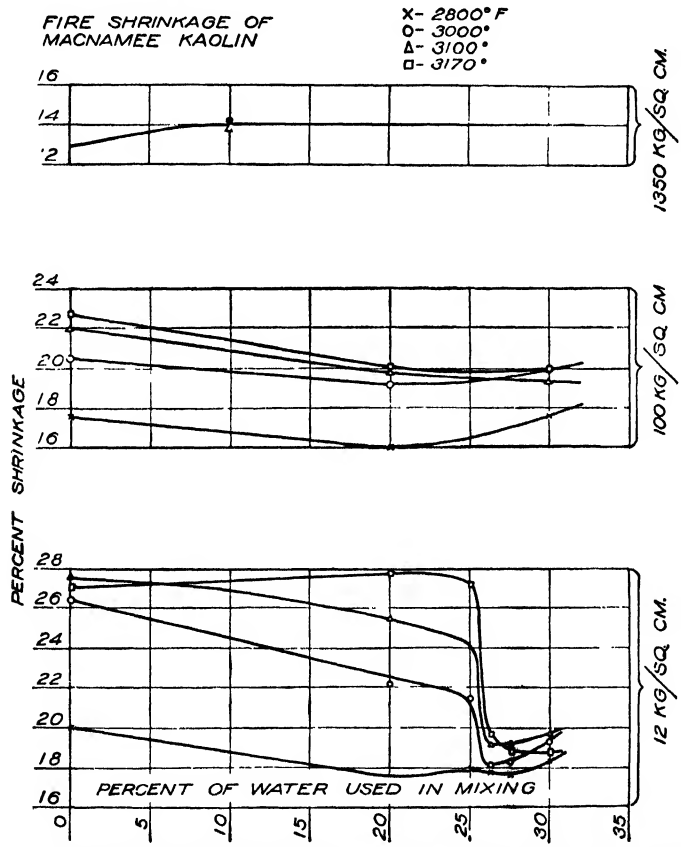

FIG. 119. Curves showing the burning shrinkage of kaolin for various water contents and molding pressures.

Bloating. Reduction of shrinkage can also take place if the clay bloats or forms bubbles in the glass owing to breaking up of sulfides, carbonates, etc. This increase in size by bloating may account for the expansion of some of the high-alumina clays and flint clays in firing, but a great deal more work needs to be done on this question before we shall know the exact mechanism causing it. Bloating, if it occurs to any great extent, is not particularly desirable, as it is hard to control and will not occur under any

appreciable load. Therefore, a shape being fired may show no change in horizontal dimensions but may shrink materially in a vertical direction.

Molding Conditions. Shrinkage is also more or less dependent on the conditions of molding, as shown by the curves in Fig. 119 for various water contents and molding pressures of kaolin and water mixtures. In fact, it will be observed that the burning shrinkage is sharply decreased by increasing the water content beyond the critical value of 25 per cent for low molding pressures. Also, the higher the molding pressure the lower is the

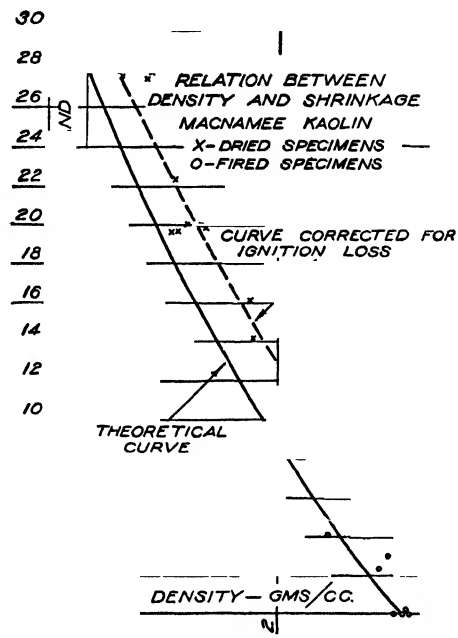

FIG. 120. Curves showing the relation between density and maximum linear shrinkage for kaolin.

burning shrinkage. For a given material, a maximum shrinkage in burning can be determined from the density of the dried or partially fired specimen (allowing for ignition loss). This is shown by the curve in Fig. 120, where the density values are plotted against the maximum linear shrinkage based on the condition of the specimen when the density is determined. This curve applies to both fired and unfired specimens. For example, if an unfired specimen has a density of 1.46, it will eventually shrink 22.0 per cent, to the condition of maximum density.

Control of Porosity. The porosity of a refractory is of great importance, as a low porosity gives better resistance to slag attack and a higher porosity, in general, gives better resistance to spalling. Also, a low-porosity material

has a high thermal conductivity, whereas a high-porosity material such as an insulating brick has a low value. It is important, therefore, that a manufacturer of refractories be able to control the porosity to suit the particular conditions for which the brick is used.

Porosity, in the same way as shrinkage, is controlled to a large extent by the molding conditions; *i.e.*, high pressures in molding give a more densely fired structure. Also, high firing temperatures give low porosities but at the same time are apt to produce distortion.

Perhaps one of the best ways of controlling porosity, especially for producing low-porosity refractories such as glass-tank blocks and slag-resisting brick, is to control the grog size carefully. This is considered so important that many modern refractory plants are controlling the grain size of a grog with great exactness. Much work has been done on the packing of grog particles to produce a structure of the lowest possible density, as noted in

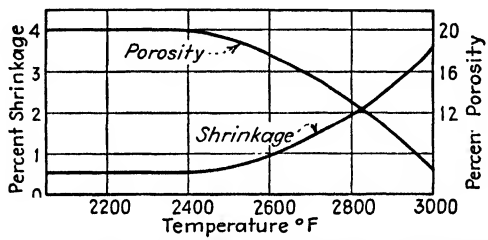

FIG. 121. Shrinkage and porosity curves for a closely packed grog having 15 per cent bond clay.

Chap. VI. Figure 121 shows the shrinkage and porosity curves for a densely packed grog body having 15 per cent of clay bond fired at various temperatures.

Chemical Control. In making certain types of refractories, it is impossible readily to obtain raw materials that are free from a certain objectionable impurity. This impurity can sometimes be converted into a non-objectionable material by adding a mineral that will combine with it and form a higher fusing compound. An example of this which was briefly mentioned before is the addition of magnesium oxide to chrome ore in such an amount that it will combine with the silica and form the mineral forsterite,[163] the highest melting compound in the magnesia-silica system.

Another example is the production of forsterite refractories, where many of the natural materials, such as olivine, produce excess silica in the form of glass or cristobalite when fired. Magnesium oxide added in the correct amount will combine with the silica to form additional forsterite.

6. Melted and Cast Refractories. For certain purposes, particularly in the production of glass-tank refractories with a minimum of porosity, it has been found desirable to produce refractories by fusing the raw mate-

rials in an electric furnace and pouring the melted refractory into a sand mold to form the desired shape. The melting process itself permits some purification of the raw materials (1) by the reduction of iron oxide to metallic iron and (2) by the elimination of some of the silica by volatilization or combination with the iron to form ferrosilicon. The casting itself is practically nonporous; and by governing the rate of cooling, the size of the crystals can be regulated as desired. This process, though comparatively expensive, seems to be justified for producing special refractories, such as mullite and alumina blocks for glass tanks.[253,254,255,258]

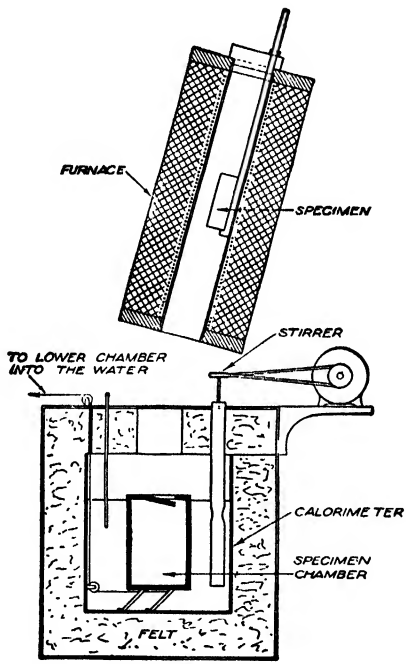

FIG. 122. Apparatus for measuring specific heat by the calorimeter method.

7. Specific Heat. The term "specific heat" has been used in the ceramic literature rather loosely and, in many cases, has been applied not only to specific heat values but to values of latent heat of association, inversion, or crystallization. Specific heat may be defined as a number expressing the ratio of the heat quantity required to raise, respectively, 1 g of the given material 1°C at a definite temperature and 1 g of water from 19.5 to 20.5°C. Specific heat can correctly refer only to the heat required for raising the temperature of a thermally stable material that is free from any changes through the measured interval. We can, therefore, correctly speak of specific heat as applying to stable refractory materials that have been

previously fired to complete all irreversible reactions and that have no reversible changes in the temperature range being measured. For example, the specific heat of quartz is continuous up to 573°C (about 1063°F), where a crystal change takes place giving off a small amount of latent heat of inversion that must be added to the specific heat to give the total heat content. The use of the term specific heat for raw clays, as is often done, is very unfortunate.

Method of Measurement. The measurement of specific heat can be carried out with considerable accuracy by the calorimeter method. In this determination, the specimen is heated in a suitable furnace to a known and uniform temperature and then dropped suddenly into a calorimeter, which can be immediately immersed in water. The heat content of the specimen is then determined by the rise in temperature of the water and the constants of the apparatus. Equipment for the high-temperature measurements of specific heat is shown in Fig. 122. This apparatus, as used by Wilkes,[283] is laid out to give a quick drop of the sample into the specimen chamber with the elimination, necessary for precise work, of splashing and steam losses.

Values. In Table 38 are given values of specific heat for a considerable number of stable refractory materials. Some of the minerals, such as quartz, cristobalite, and zirconia, have reversible inversions, but these are small in effect and are included by the experimenter in the value for specific heat.

8. Heat Quantity Required to Raise the Temperature of Clays and Ceramic Bodies. *Method of Measurement.* The determination of the heat required to raise a clay to a certain temperature is a very difficult measurement because the calorimeter method, which can be used for stable materials, is not applicable here. The heat given up on cooling is quite different from the heat absorption in raising the temperature. It is, therefore, necessary to find some way of actually measuring the heat going into a given specimen as it is raised through definite temperature intervals. A number of methods have been used to make these measurements; but because of the inherent difficulties of measuring the heat directly absorbed by the specimen, the results are not highly precise, and a great deal of work is still to be done in this field before we will feel sure of the values.

One of the methods, used for this purpose by Navias,[271] consists in heating the specimen of clay with a surrounding platinum coil, which is, in turn, enclosed in a vacuum jacket to prevent possible escape of heat to the outside. Nevertheless, during the rather long period of test, some heat is lost. This is measured by immersing the vacuum jacket in a water bath, which permits the heat escaping to be measured. By calibrating this apparatus with a material of known specific heat, the proportion of heat going into the sample and the proportion going into the container, coil, etc.,

TABLE 38. VALUES OF MEAN SPECIFIC HEAT

Material	Temperature range, °C.	Mean specific heat	Investigators
Alumina, fused	20–200	0.211	W. Cohn[374]
	20–400	0.231	
	20–600	0.251	
	20–800	0.272	
	20–1000	0.304	
Alumina, pure	30–100	0.206	G. B. Wilkes[382]
	30–300	0.226	
	30–500	0.240	
	30–700	0.250	
	30–900	0.258	
	30–1100	0.265	
	30–1300	0.271	
	30–1500	0.276	
	30–1700	0.280	
Cristobalite	0–200	0.213	R. Wietzel[389]
	0–400	0.242	
	0–800	0.260	
	0–1600	0.276	
Chrome brick	30–218	0.178	Y. Tadokoro[388]
	30–318	0.195	
	30–382	0.210	
	30–480	0.216	
	30–579	0.221	
	30–894	0.215	
Fireclay brick—35 per cent Al_2O_3	25–600	0.228	Bradshaw and Emery[267]
	25–1000	0.265	
	25–1200	0.284	
	25–1400	0.297	
Fireclay brick	600	0.227	J. W. Mellor and others
	1000	0.263	
	1200	0.262	
Fireclay brick	200	0.204	E. Heyn and others[264]
	400	0.222	
	600	0.236	
	800	0.248	
	1000	0.256	
	1200	0.263	
Lime, fused	375–400	0.181	P. N. Laschtchenko
	590–680	0.193	
Magnesia, pure	30–100	0.234	G. B. Wilkes[382]
	30–300	0.247	
	30–500	0.259	
	30–700	0.269	
	30–900	0.277	
	30–1100	0.283	
	30–1300	0.288	
	30–1500	0.291	
	30–1700	0.294	
	30–1800	0.295	
Magnesite brick—88 per cent MgO	25–605	0.265	A. T. Green[270]
	25–825	0.274	
	25–930	0.280	
	25–1041	0.285	
	25–1115	0.292	
Mullite, $3Al_2O_3 \cdot 2SiO_2$	20–200	0.161	W. Cohn[373]
	20–400	0.167	
	20–600	0.173	
	20–800	0.175	
Porcelain fired	20–200	0.195	W. Cohn[373]
	20–400	0.212	
	20–600	0.232	
	20–800	0.264	
	20–1000	0.304	

TABLE 38. VALUES OF MEAN SPECIFIC HEAT (*Continued*)

Material	Temperature range, °C.	Mean specific heat	Investigators
Quartz glass, SiO_2	0–200	0.201	R. Wietzel[269]
	0–400	0.223	
	0–600	0.239	
	0–800	0.251	
	0–1000	0.258	
	0–1200	0.262	
	0–1400	0.269	
	0–1600	0.278	
Quartz, crystalline, SiO_2	0–200	0.203	R. Wietzel[269]
	0–400	0.223	
	0–800	0.259	
	0–1600	0.271	
Silica brick	25–600	0.226	Bradshaw and Emery[267]
	25–1000	0.263	
	25–1200	0.282	
	25–1400	0.293	
Silicon carbide, crystalline, SiC	0	0.140	O. Weigel[265]
	200	0.233	
	400	0.277	
	600	0.275	
	800	0.225	
	1000	0.129	
Spinels:			
Ferrous aluminate, $FeO \cdot Al_2O_3$	50–1025	0.25	Parmelee[175]
Magnesium aluminate, $MgO \cdot Al_2O_3$	50–1025	0.29	Parmelee[175]
Magnesium aluminate, $MgO \cdot Al_2O_3$	0–243	0.214	A. E. MacGee[276]
	0–399	0.229	
	0–534	0.232	
	0–632	0.250	
	0–783	0.255	
	0–886	0.255	
	0–1042	0.257	
Zinc aluminate, $Zr \cdot Al_2O_3$	50–1025	0.22	Parmelee[175]
Ferrous chromite, $FeO \cdot Cr_2O_3$	50–1025	0.20	Parmelee[175]
Magnesium chromite, $MgO \cdot Cr_2O_3$	50–1025	0.22	Parmelee[175]
Manganese chromite, $MnO \cdot Cr_2O_3$	50–1025	0.18	Parmelee[175]
Zinc chromite, $ZnO \cdot Cr_2O_3$	50–1025	0.18	Parmelee[175]
Ferrous ferrite, $FeO \cdot Fe_2O_3$	50–1025	0.23	Parmelee[175]
Magnesium ferrite, $MgO \cdot Fe_2O_3$	50–1025	0.20	Parmelee[175]
Manganese ferrite, $Mn \cdot Fe_2O_3$	50–1025	0.21	Parmelee[175]
Zinc ferrite, $ZnO \cdot Fe_2O_3$	50–1025	0.17	Parmelee[175]
Zirconia—99 per cent, ZrO_2	25–600	0.137	Bradshaw and Emery[267]
	25–1000	0.157	
	25–1200	0.167	
	25–1400	0.175	

can be calculated. A test is then made by heating the given sample to a certain temperature and holding it there until equilibrium is reached, the heat input being measured by the number of watts supplied to the heater. The temperature is again raised to another level; the additional heat input measured; etc. From these values, a curve of heat input against temperature can be plotted.

White[266] and Cohn[274] supported a specimen of the clay in a small container in the center of a wire-wound furnace and determined the heat passing from the furnace wall to the specimen by the temperature difference

TABLE 39. THE HEAT REQUIRED TO BURN UNFIRED BODIES

Material	Temperature, °C.	Cal.* to heat 1 g. from 20° to t°C.	Investigators
Ball clay (Kentucky)	0–200	68	A. E. MacGee[275]
	0–400	159	
	0–600	285	
	0–800	366	
	0–1000	465	
Diaspore clay	0–200	70	A. E. MacGee[276]
	0–400	150	
	0–600	274	
	0–800	350	
	0–1000	450	
Firebrick body	0–200	68	A. E. MacGee[275]
	0–400	145	
	0–600	268	
	0–800	337	
	0–1000	415	
	0–1200	507	
Fire clay, raw Chamotte	200	35	W. Cohn[272]
	400	80	
	600	201	
	800	243	
	1000	326	
	1200	452	
	1400	572	
Kaolin, Georgia	0–200	79	A. E. MacGee[275]
	0–400	183	
	0–600	332	
	0–800	402	
	0–1000	496	
Kaolin, Zettlitz	200	37	W. Cohn[272]
	400	86	
	600	241	
	800	333	
	1000	420	
	1200	489	
	1400	560	
Porcelain body (green)	200	34	W. Cohn[272]
	400	81	
(Clay substance, 55 per cent)	600	193	
(Quartz, 22.5 per cent)	800	248	
(Feldspar, 22.5 per cent)	1000	331	
	1200	428	
	1400	528	

* In the cases noted the initial temperature is 0°C.

between the specimen and the furnace. By calibrating this apparatus with a specimen of known specific heat, the heat input for any given specimen can be computed.

MacGee[275] used a differential thermal method in which a specimen of the clay and a specimen of a neutral substance of known specific heat were placed side by side in a wire-wound furnace. A differential thermocouple recorded the difference in temperature between the two specimens, from which the heat input to the clay sample through any temperature interval could be computed.

Perhaps one of the most satisfactory methods, but one that has not as yet been applied extensively to clays, is that suggested by Smith[286] in which a comparatively thick-walled refractory crucible is placed in the center of a wire-wound furnace with the clay sample inside it. A differential thermocouple with the junctions, respectively, on the inside and the outside surface of the crucible is connected to a temperature controller, which raises the furnace at such a rate that a definite temperature difference is always present in the walls of the crucible. The heat input to the sample is always constant for given time intervals, assuming no change in conductivity with small temperature changes. Therefore, a plot of furnace temperature against time will enable a curve of heat input against temperature to be established. It should be noted that unlike the other methods, calibration factors are not necessary provided the thermal conductivity of the crucible wall is known.

A recent paper by Shorter[287] makes a critical survey of the subject and analyzes the methods of MacGee and of Cohn.

In Table 39 will be found values for the heat required to raise various types of clays and ceramic bodies to definite temperature levels.

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CHAPTER IX

KILNS FOR BURNING REFRACTORIES

1. Introduction. We know that kilns have been used by man for many thousands of years, as their remains are frequently found in the excavations of ancient sites of early civilization. These primitive kilns were of the updraft type and, in most cases, consisted only of a firing chamber, a perforated floor, and a wall. The construction of a permanent kiln

FIG. 123. A Chinese kiln with a number of sections. It is lighted at the bottom, the waste gases preheating the higher chambers, and the cooling of the lower chambers preheating the combustion air. The fuel is small chips of dry wood fed through the holes in the crown. (*Henry Jewett Greene.*)

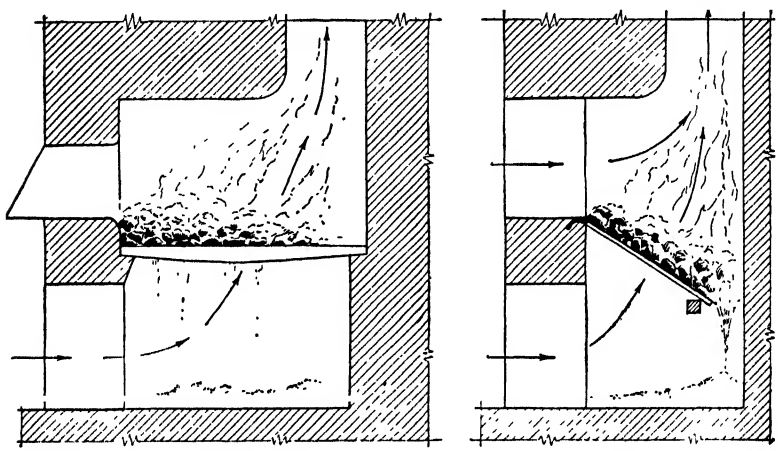
roof was too much of a structural problem for most of the early potters, and recourse was made to a temporary roof of green poles and raw clay, which would hold in place long enough for the very low temperature of firing used at that time. There is, however, one exception, as a kiln has recently been found in Tepe Gawra that was believed to have had a permanent roof at a period as early as 4500 to 4000 B.C.

The early Chinese kilns, which consisted of a series of chambers extending up the side of a hill, were remarkably similar to our modern chamber kilns and permitted a considerable degree of recuperation as the fire

advanced from one chamber to another. An interesting kiln of this type is shown in Fig. 123.

It should be remembered that in dealing with these early kilns as well as our modern ones, four essentials must always be present: (1) a means for producing the heat, (2) a support for the ware, (3) a container such as the walls and crown to confine the heat in the working space, and (4) a means to transfer the heat from the source to the ware.

2. General Principles. *Production of Heat.* As the majority of refractories are fired with coal as a fuel, this method of heating will be discussed first. Coal is used because of its low cost and because most of the refrac-



(*a*) (*b*)

FIG. 124. Kiln furnaces with flat and sloping grates.

tories are not particularly sensitive to impurities in the kiln gases that might arise from using coal as a fuel. The coal is generally burned in furnaces with sloping or flat grates as shown in Fig. 124. The air for combustion passes partly through the fuel bed and partly over the top, the hot gases generally going upward into the kiln over a bag wall, as shown in Fig. 125. In the round or rectangular kilns, a considerable number of furnaces are spaced around the wall of the kiln in order to distribute the heat as evenly as possible.

The manufacturers of refractories generally prefer for their kilns a good grade of bituminous coal giving a long flame; also a low ash content and a high fusion point of the ash is desirable. In most cases, it is necessary to have a low sulfur content so that sulfates will not deposit on the surface of the bricks during the water smoking period.

It has been the practice to fire the coal by hand, although recently mechanical stokers are being used to a considerable extent.

Many of the coal-fired kilns waste a good deal of heat as a result of radiation from the more or less open fire mouths and escaping gases from the fire bed that are not pulled into the kiln by the draft. These condi-

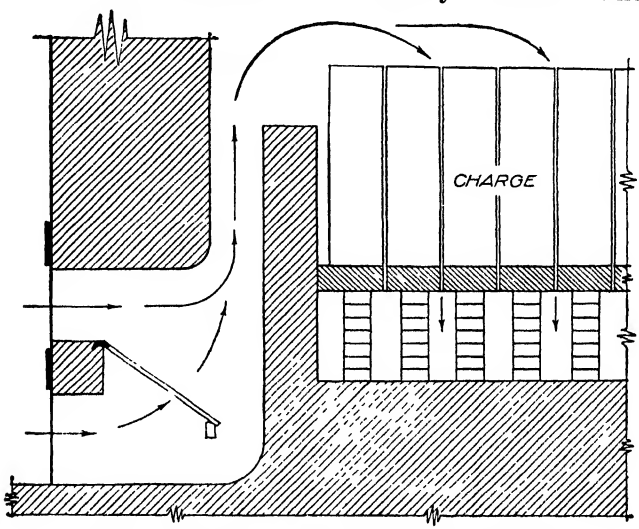


FIG. 125. Passage of gases through a downdraft kiln.

tions have been improved in some of the modern installations by tighter doors and forced draft.

Oil has many advantages as a fuel for firing refractories; and in some localities, the cost compares favorably with coal. Advantages of oil are a

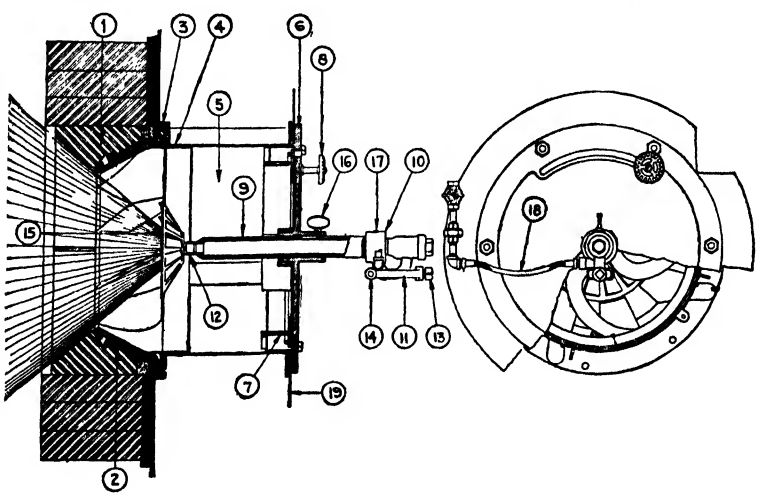


FIG. 126. A mechanical atomizing burner *(Courtesy of Babcock and Wilcox Company.)*

more perfect temperature control, the possibility of a higher maximum temperature, a generally cleaner kiln atmosphere, and a smaller labor requirement for the firing operation. Oil is, of course, obtainable in a number of different grades; but from the cost standpoint, the heavier grades of oil, such as Bunker C, are generally used. A number of different types of burner are available for firing with oil. In principle, they all break the oil up into a spray of fine particles and intimately mix them with the combustion air. In burners of the mechanical atomizing type, as shown in Fig. 126, the oil is atomized by forcing it through a fine orifice at relatively

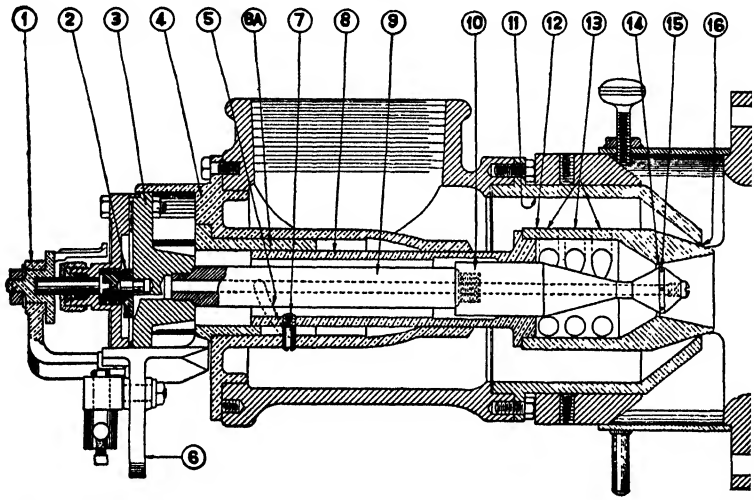


FIG. 127. An air-atomizing oil burner. (1) Oil-control valve lever. (2) Oil-control valve cam. (3) Oil-control valve consisting of a V-groove in a flat surface. (4) Burner backplate. (5) Curved slot. (6) Operating lever. (7) Inner-nozzle operating pin. (8) Inner air-nozzle operating tube. (9) Oil tube. (10) Oil nozzle. (11) Outer air nozzle. (12) Inner air nozzle. (13) Primary air-supply openings. (14) Primary air discharge. (15) Oil nozzle. (16) Secondary air-discharge opening. (*Courtesy of Hauck Manufacturing Company.*)

high pressure. This method is particularly suitable for burners of high capacity, as the orifice becomes very tiny for small burners and there is apt to be danger of particles getting through the filter and plugging the orifice.

Oil is also fired in air- or steam-atomizing burners where high-pressure air or steam is used to inject the oil into the kiln and at the same time break it up into a fine mist. Secondary air is generally supplied from a low-pressure source. A burner of this type is shown in Fig. 127. In setting up an oil-burning system, care should be taken that it be properly laid out to ensure reliable operation. The heavier oils have to be heated and must be kept hot until they actually reach the burner; otherwise the viscosity will become so great that proper atomization is impossible. A

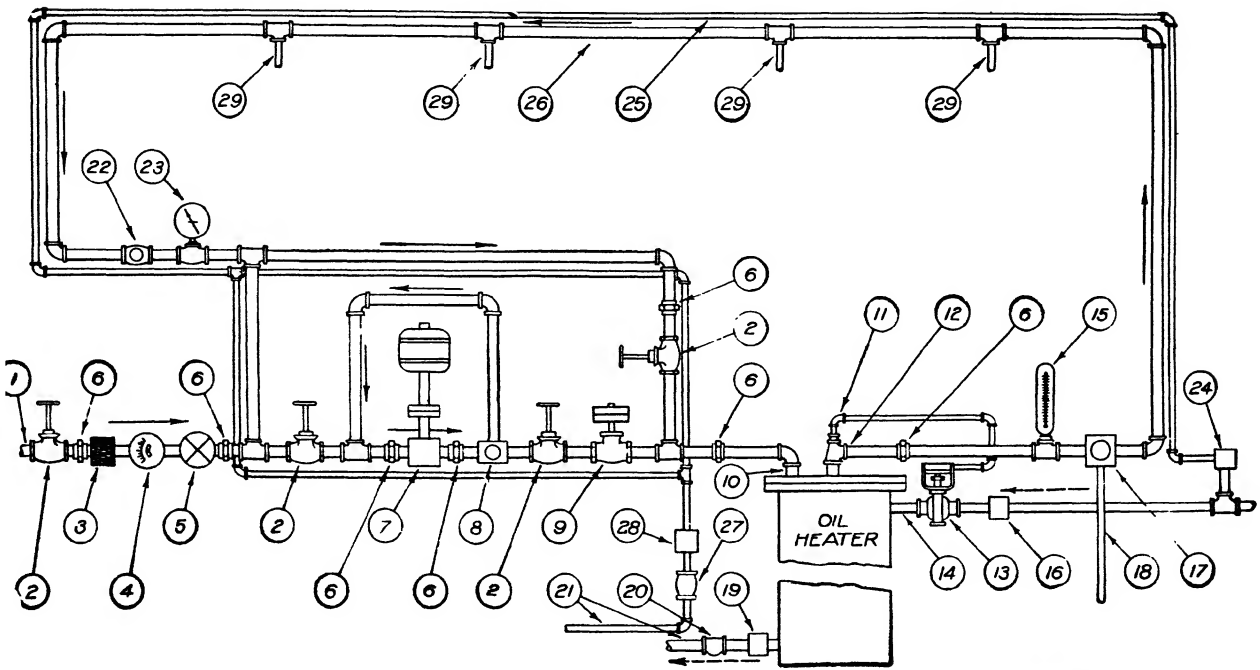


FIG. 128. A complete oil-burner installation. (1) Supply line from oil system. (2) Globe valve. (3) 2-in. edge plate oil filter. Type EF 250 lb. (4) Buffalo oil meter. (5) Reducing valve. (6) Standard union. (7) Hauck 300 gph circulating-oil pump. (8) Pressure relief valve, 1-in. size. (9) Automatic oil shut-off valve. (10) Oil inlet to oil heater. (11) Automatic oil-temperature control. (12) Oil outlet from oil heater. (13) Automatic oil-temperature steam control. (14) Steam inlet to oil heater. (15) Oil thermometer. (16) Fisher strainer, ¼-in. size, Type 260. (17) Relief valve, 1-in. size. (18) Relief oil line to sump or barrel. (19) Fisher strainer, ⅜-in. size, Type 260. (20) Fisher steam trap, ⅜-in. size, Type ST. (21) Condensate discharge to sump. (22) Check valve. (23) Oil pressure gage. (24) Steam-pressure reducing valve, 50 to 5 lb. (25) Steam-tracer line, ½-in. iron pipe or copper tubing. (26) Loop oil line to burners. (27) Steam trap, ½-in. size, Type ST. (28) Fisher strainer, ½-in., size, Type 260. (29) Leads to burners. (*Courtesy of Hauck Manufacturing Company.*)

good filter that will permit cleaning without shutting down the oil flow is necessary, and often a complete recirculating system is desirable. In Fig. 128 is shown a layout for an oil-fired kiln that has been found quite satisfactory.

In regard to the arrangement of the burners in the kiln, they may fire over the charge in a downdraft kiln, as shown in Fig. 129, or they may fire against the side of the charge, preferably through a checker brick to distribute the heat, as shown in Fig. 130. In setting up the burner, care must be taken to allow sufficient combustion space for the particular burner used; otherwise carbon will tend to build up on the surfaces around the

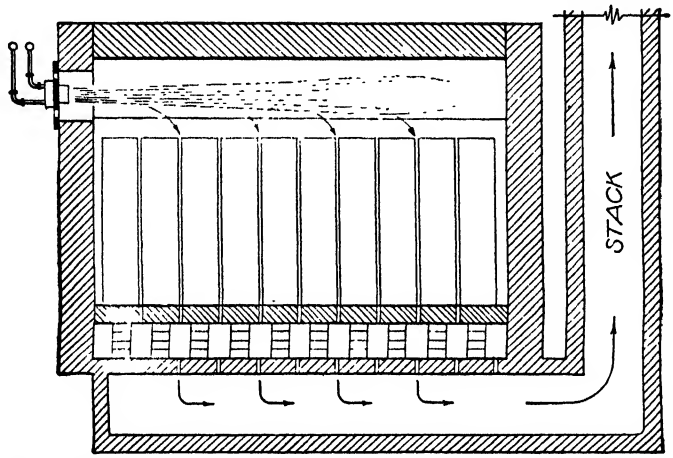


FIG. 129. An oil-fired kiln in which the flame passes above the charge.

flame. The recommendations of the burner manufacturers should be followed when the combustion chamber is laid out.

Natural gas is an excellent fuel for burning refractories, but in only a few localities is it sufficiently plentiful to make its use economical. It has the advantage of making temperature control a simple problem, and the heat produced is very clean. In general, the burner cost for a gas installation will be found less than that for burning oil.

Producer gas is used to some extent in firing kilns, especially in Europe. In most cases, the gas is used hot and without scrubbing; consequently provision must be made for draining and cleaning the connecting pipes between the producer and the burner, as they periodically fill up with tar and soot. In regions where only low-grade coal is available, the producer-gas firing is found to be quite successful. The producer gas gives a comparatively low-temperature flame, so there is little danger of overheating any part of the charge; and as the volume of gas is large because of this

low heat value, it tends to give an even temperature throughout the kiln. The small-unit gas producer has been steadily improved and is a much more reliable and efficient piece of equipment than it was in the past.

There is not space here to go into the principles of combustion, but it should be remembered that the amount of excess air used is of the greatest importance in all kiln firing. The greatest combustion efficiency is reached with very low amounts of excess air; but on the other hand, a large volume flow of gases is needed to carry out the moisture in the water-smoking stage of firing, to provide uniformity of temperature, and to supply

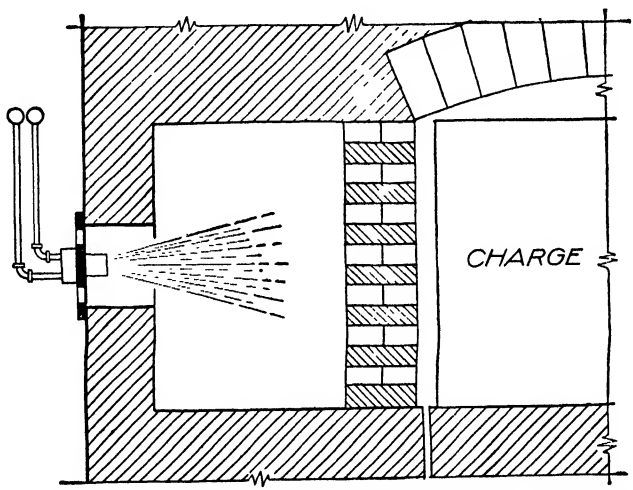


FIG. 130. A kiln in which the oil flame passes through a checkerwork.

enough oxygen to burn away carbonaceous matter. Some of the properties of a typical combustion gas are shown in Table 40.

There is a considerable saving of fuel when preheated air is used. Preheat is seldom used, however, in periodic kilns. In the case of chamber and tunnel kilns, preheat temperatures as high as 2000°F (about 1100°C) are reached with a real saving in fuel. Preheating is used in some cases to attain higher temperatures than would be possible with cold air. The reduced price of commercial oxygen in the last few years also makes possible its addition to the combustion air to aid in reaching high temperatures.

Because of its high cost, electric heating is not used to any extent for firing refractories. An exception to this is the firing of small pieces, such as spark-plug porcelains. A considerable amount of research has been carried out in the last few years to produce resistors for high-temperature electric firing.[6] The most used elements are, of course, the silicon-carbide rods capable of giving a fairly long life up to temperatures of 1500°C

TABLE 40. PROPERTIES OF TYPICAL COMBUSTION GAS AT ATMOSPHERIC PRESSURE

Temperature		Relative volume	Specific heat at constant pressure	Viscosity, poises
°C.	°F.			
0	32	1.0	0.22	170×10^{-6}
100	212	1.3	0.22	220
200	392	1.7	0.23	260
300	572	2.0	0.24	290
400	752	2.3	0.25	320
500	932	2.8	0.25	350
600	1112	3.1	0.26	370
700	1292	3.4	0.26	390
800	1472	3.8	0.27	410
900	1652	4.2	0.27	430
1000	1832	4.6	0.28	450
1100	2012	4.9	0.28	460
1200	2192	5.3	0.29	480
1300	2372	5.7	0.30	490
1400	2552	6.1	0.30	500
1500	2732	6.5	0.31	510
1600	2912	6.8	0.32	510
1700	3092	7.2	0.33	520
1800	3272	7.5	0.34	520
1900	3452	7.9	0.35	530
2000	3632	8.3	0.36	530

(about 2730°F). Molybdenum rods sealed in porcelain or sintered alumina[74] tubes have been experimented with in Germany but apparently were not commercially successful. Work at TVA indicated some promise with carbon rods enclosed in porcelain tubes with a reducing atmosphere. The Nernst resistor, composed of oxides having a low electrical resistance at high temperatures, can be used up to 2000°C (about 3600°F). However, they are costly and have to be initially heated from a separate source.

Transfer of Heat. One of the most difficult problems in kiln design is to transfer the heat efficiently from its source to the ware. The problem is unusually difficult in the kiln because the ware is in small units stacked into a considerable volume and therefore radiant-heat transfer, so important in furnaces such as those used in the metallurgical industry, can play little part. For the same reason, conduction of heat into a bulky charge of small units is of little consequence. Therefore, we must rely almost entirely upon convection for heating of the charge.

The transfer of heat from a moving stream of gas to a solid surface is well understood. The transfer rate depends mainly on the temperature

difference between the gas and solid and the velocity with which the gas is passing by the solid. The curves in Fig. 131 give an idea of the rate of heat transfer under different conditions between a gas and a solid. The transfer of heat from the moving gas by radiation from the gas itself and the incandescent particles that it contains is quite important in furnaces of large volume and great flame thickness, such as would be found in the glass-tank or open-hearth furnace; however, in the kiln, where the gas stream is divided into relatively thin layers, this radiation cannot play a very important part, although attempts are made in practice to use

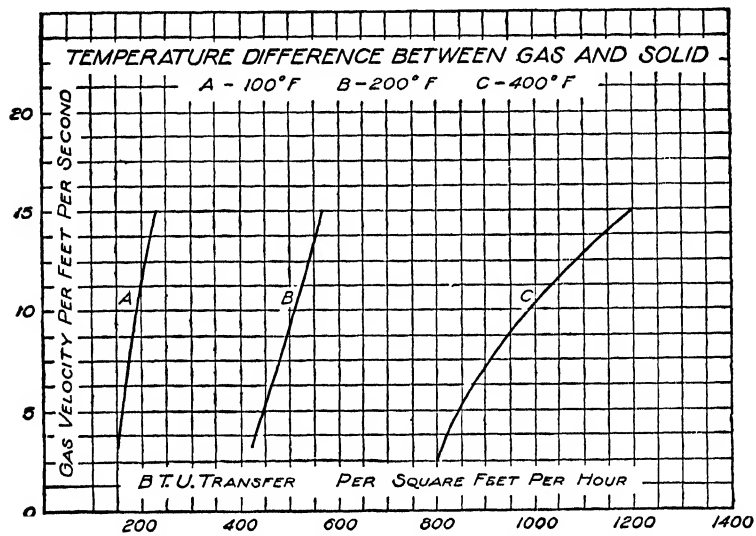


FIG. 131. Rate of heat transfer between a gas and a solid.

long-flame coal to bring the heat down to the bottom of the charge of a downdraft kiln.

Equalization of Temperature. One of the most important problems in kiln design is to produce a uniform temperature throughout the volume of the charge. This is by no means an easy matter, as few large periodic kilns now operating show a difference of less than 50°F from top to bottom of the charge. In tunnel kilns, with their small cross section, the temperature uniformity is better, but here again it is apt to vary from place to place in the car by an appreciable amount.

Considering first the case of a downdraft kiln under equilibrium conditions, it may be readily shown that the temperature difference between top and bottom is related to the mass flow of gases. In Fig. 132, the section AA may represent the top of the charge and BB the bottom. If M equals the weight of gases flowing through the channel in a unit time

and S the heat lost between AA and BB by transfer laterally through the walls per unit time, then

$$S = (t_1 - t_2)c_p M$$

$$t_1 - t_2 = \frac{S}{c_p M}$$

where c_p = the specific heat of the gas
t_1 and t_2 = the temperatures of AA and BB, respectively

We may therefore conclude that a more even temperature is obtained by a large volume flow, which may be realized by the addition of excess air to the products of combustion. This equation also shows that insulation of the kiln side walls will give a more even vertical temperature distribution.

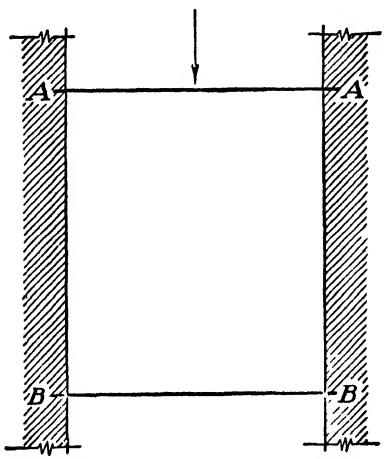


FIG. 132. The effect of flow velocity on temperature distribution.

Another method of equalizing the temperature and one that is theoretically very attractive is the recirculation of the combustion gases through the charge. In this way, a large volume flow is obtained, thus decreasing the temperature difference; while at the same time, the volume of gases leaving the kiln is relatively small. The only difficulty with the recirculation method is the practical problem of handling the high-temperature gases. At the lower temperatures encountered in heat-treating furnaces, gases can be recirculated with water-cooled, alloy fans at temperatures close to 1800°F (about 980°C); but above this, the only possible means is by injector action, a method quite successful in driers but one that has not been developed for kilns at the present time. Recently, recirculation has been used successfully in some tunnel kilns at the preheating end.

The equalization of temperature at right angles to the path of flow is readily accomplished by adjustments in the floor openings, so that the hotter areas have the openings reduced and the cooler areas have them enlarged. By trial and error, a very uniform temperature can be attained over the horizontal cross section of the charge.

One often hears the kiln fireman state that he uses a damper or a close-set floor to back up the heat in the kiln and give a more uniform temperature. It is not generally understood, however, just what the effect of dampers and restrictions to the flow accomplish. The curves in Fig. 131

show clearly the great increase in heat transfer from the gas to the charge with increasing velocities. The point in the kiln where the flow is restricted has an increased velocity, and thereby more heat is transferred from the gas to the charge. As the usual problem is to raise the temperature at the bottom of the charge, it is possible to have a relatively open setting in the charge itself and as small floor openings as are permitted by the available draft. Owing to the high velocity through the floor openings, the heat from the gas will be given up to a much greater extent at the floor than in the other parts of the charge and will therefore tend to compensate for the gradual cooling of the gas as it goes down through the charge.

Temperature uniformity can be attained in a muffle kiln by varying the area of contact of the gas with the muffle wall from the burner to the exit point; *i.e.*, at the burner, the passage for the gas would only have a small width in contact with the muffle, whereas in the exit, it would have a large width. By properly adjusting these areas, a muffle kiln with absolute uniformity of temperature can be constructed. Laboratory kilns that have been made in this way, though bottom fired, show a temperature at the top of the muffle within a few degrees of the bottom temperature.

Insulation of the kiln tends to increase the uniformity of inside temperature, because (1) it tends to keep the inside walls of the kiln at a more uniform temperature, and because (2) an insulated kiln requires less fuel and therefore the gases entering the kiln can be at a lower temperature. Also, as explained from the diagram in Fig. 132, the insulation of the walls of the kiln increases the uniformity of temperature by minimizing the heat loss as the gases pass through the charge.

Kiln Efficiency. The efficiency of the kiln is usually defined as the ratio of the heat required to bring up the ware to its maximum temperature divided by the amount of heat supplied by the fuel. This definition is perfectly logical when applied to the periodic kiln; but when it is used under conditions where recuperation occurs, then it may become absurd, as efficiencies of over 100 per cent have been determined on actual kilns. This can perhaps be made clear by the set of heat-balance diagrams shown in Fig. 133 beginning with a nonrecuperative kiln and ending with one having a high recuperative effect. It will be seen that the heat required to bring the ware up to temperature is the same in each case but the external heat supplied to the kiln becomes progressively smaller as the recuperative action increases. It would seem more reasonable to give fuel consumption per thousand standard-sized bricks rather than to express efficiency in percentage.

It should be stated here that a high degree of kiln efficiency is often incompatible with good uniformity of temperature because high efficiency demands a low temperature of exit gases and these, in turn, mean a low

temperature of the charge in the bottom of the kiln. Only by recuperative action or recirculation can good temperature uniformity be obtained together with high efficiency.

It is obvious that the insulation of kilns will increase their efficiency, but unfortunately very few data are at hand to show just what the saving might be, as there is seldom an opportunity to compare similar kilns, one of which is insulated and the other not. It should be brought out, however,

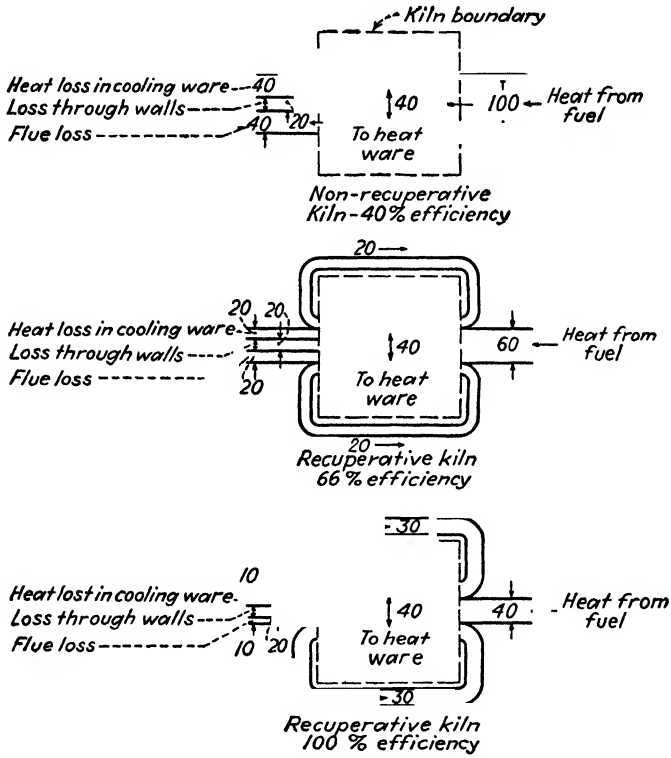


FIG. 133. Heat balance diagrams.

that the effect of insulation is not only to reduce the heat passing through the walls and the crown of the kiln but also to reduce the volume of exit gases in proportion. This fact is little understood, and it may be well to emphasize it with an example, under steady temperature conditions, in Table 41. This follows because, for a constant exit temperature, the heat lost in the flue gases is proportional to the heat input.

3. Periodic Kilns. The periodic kiln has been much used in the refractories industry. Its advantages are a comparatively low first cost and flexibility in operation. The disadvantages are the poor fuel economy

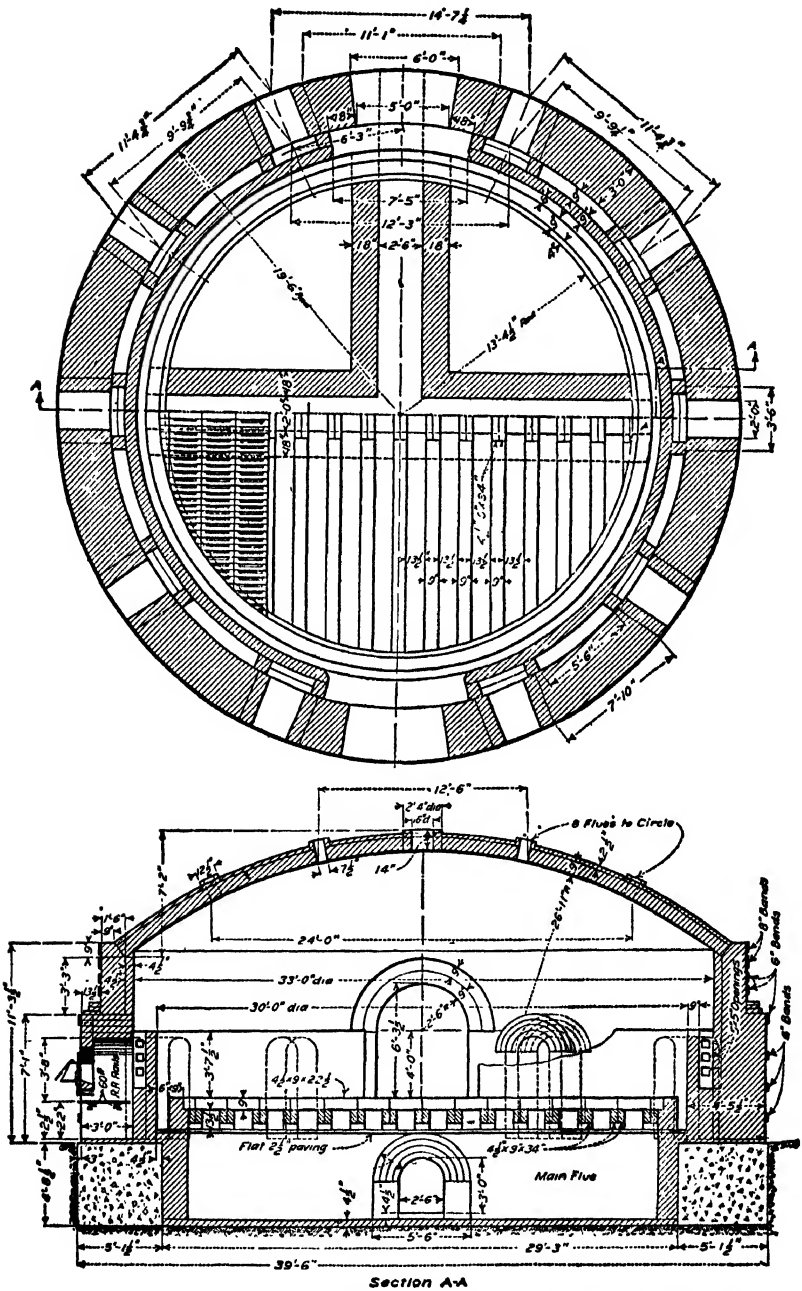


FIG. 134. A round downdraft kiln for firing refractories. (*J. Am. Ceram. Soc.*)

TABLE 41. SAVING DUE TO INSULATION

	Uninsulated kiln	Insulated kiln	
		As usually computed	As it occurs
Heat passing through walls, B.t.u....	50,000	25,000	25,000
Heat lost in flue gases, B.t.u.....	50,000	50,000	25,000
Heat supplied to the kiln, B.t.u.....	100,000	75,000	50,000
Heat saved, per cent.....	0	25	50

secured, the unevenness of temperature when the charge is piled high, and the strain on the brickwork due to the repeated heating and cooling. Although the periodic kiln is being gradually displaced by the tunnel kiln, it will always be used to some extent for burning large shapes and special bricks.

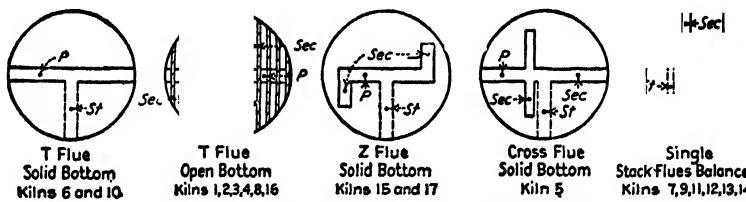


FIG. 135. Flue arrangements for downdraft kilns.

Common Types of Kilns. The periodic kiln generally used to fire refractories is either of the circular downdraft type or of the rectangular type. The former is usually preferred because of the low cost for a given capacity and the even temperature distribution possible. The round kilns are made in sizes of 26 to 42 ft inside diameter, but sizes from 30 to 36 ft are generally preferred. The capacity ranges from 30,000 to 140,000 nine-inch equivalents. The fireboxes are arranged around the kiln and vary in number from 8 to 18 according to the size and type. The construction of the walls and crown is practically the same in all cases, but there is a great diversity of arrangements for the floor and flues.

In Fig. 134 is shown a well-designed, round, downdraft kiln for burning refractories. It will be noted that the flues are arranged in such a way as to give an even draft at all parts of the floor. Figure 135 gives a number of other flue arrangements that are sometimes used.

Although there is considerable variation in the dimensions of this type of kiln, the figures in Table 42 are generally used. It is generally considered good practice to connect two or four kilns to a single stack having

separate flues for each kiln. This method gives a hot stack under all conditions, so that a good draft is produced when starting a kiln. The height of stack generally varies from 30 to 40 ft.

TABLE 42. KILN AREAS

Floor to top of crown, ft.	11–19
Height of bag wall above floor, ft.	3–5
Area of floor openings, per cent of floor area	2.8–10
Area of grates, per cent of floor area	8–12.6
Area of main flue, per cent of floor area	1.4–3
Area of stack, per cent of floor area	1–1.6

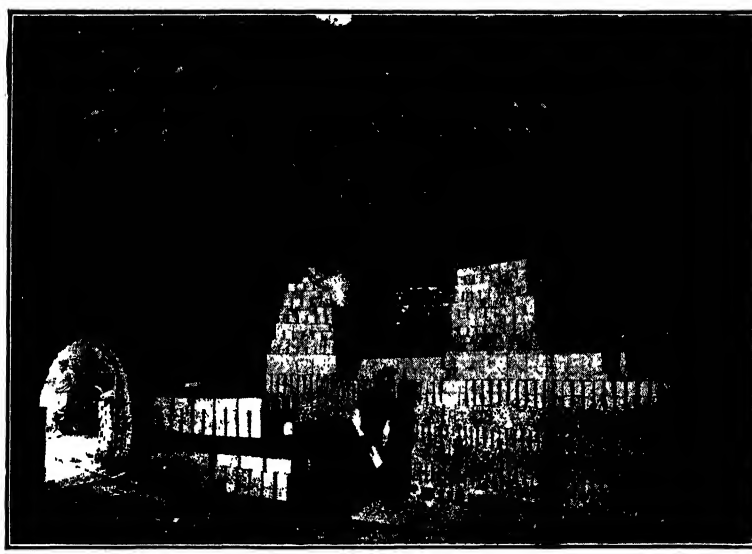


FIG. 136. A typical kiln setting. (*Courtesy of Harbison-Walker Refractories Company.*)

Usually the turnover time in this type of kiln, burning clay refractories, is approximately 14 days: 4½ days for firing, 5½ days for cooling, 2 days for drawing, and 2 days for setting. When burning silica brick, the kiln is held at the maximum temperature for some length of time, so the turnover time is somewhat longer. A typical kiln setting is shown in Fig. 136.

The modern tendency seems to be toward the use of blowers and suction fans to accelerate the burning and cooling. In this way, as much as 50 per cent can be taken off the burning and cooling time, which means a marked increase in the output of the kiln. There is, however, a limit to the rate of firing, caused by the burning properties of the clay used. On the other hand, the cooling rate is limited because of the strains set up in the kiln itself by a too rapid change in temperature.

There are a number of other types of periodic kilns for burning refractories, but they are not so generally used. Descriptions of them can be found in the references given at the end of this chapter.

Fuel Consumption. The fuel consumption of periodic kilns is comparatively large and varies with the burning temperature and the amount of insulation used on the kiln. In Table 43 are given some figures on the fuel used in a number of periodic kilns.

TABLE 43. FUEL CONSUMPTION OF PERIODIC KILNS

Type of kiln	Capacity, 9-in. equivalents	Fuel	Maximum temperature		Firing time, hr	Fuel per 1,000 bricks (9-in. equivalents)
			°C	°F		
Round downdraft	65,000	Coal	1270	2318	192	2,200 lb
	32,000	Coal	1290	2350	150	1,450 lb
	60,000	Coal	1320	2408	156	1,200 lb
	48,000	Coal	1170	2138	132	1,500 lb
		Coal		2600		3,000 lb
		Coal	1150	2100		2,100 lb
		Coal	1250	2280		2,500 lb
		Coal	1316	2400		2,400 lb
Rectangular downdraft	42,000	Coal	1280	2336	163	1,770 lb
	60,000	Coal	1270	2318	168	1,800 lb
Round downdraft	76,000	Oil	1270	2318	110	125 gal
		Oil	1400	2550		115 gal
Rectangular (insulated) downdraft	10,000	Oil	1650	3000	115	400 gal
	5,000	Oil	1650	3000	100	500 gal
Round downdraft	50,000	Natural gas	1250	2280	216	18,000 cu ft

The heat losses in periodic kilns are mainly in the flue gases, as shown in Table 44, which gives average figures for periodic kilns burning fireclay bricks with coal.

Setting Methods. The method of setting the brick in the periodic kiln depends on their shape, the type of refractory, and individual plant practice. The setting is usually in a checkerwork pattern, with about ½ in. between bricks, making up a bench extending across the kiln. For straight bricks, this means three set across three others. To prevent the bricks from sticking to one another, silica sand is sprinkled on the top of the bench before placing the next pieces. Brick such as magnesite and

chrome cannot support themselves in a high setting and therefore are commonly boxed with silica brick, which carry the load.

TABLE 44. HEAT BALANCE OF A TYPICAL PERIODIC KILN

	Per Cent
Heat to raise temperature of bricks, or efficiency	15–45
Heat to drive off moisture	0–3
Heat in combustion of ash	4–10
Heat in combustion in flue gases	0–5
Heat in dry flue gases	20 45
Heat in water vapor in gases	4–7
Heat to raise temperature of kiln walls	4–15
Heat to raise temperature of kiln crown	2 4
Heat lost by walls and crown	3–9
Heat lost in bottom and flues	4–12

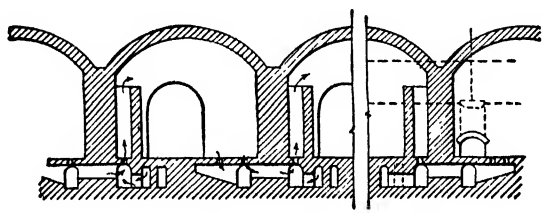


FIG. 137. Section of a typical compartment kiln.

4. Continuous Compartment Kilns. The compartment kiln is designed to provide more economical operation than can be given by the periodic kiln. A great number of methods are used, but the general principle is the same in all cases. In Fig. 137 is shown a portion of a typical compartment kiln. Each chamber is similar to a downdraft periodic kiln; but instead of the gases passing out of the stack, they pass from one chamber to the bag wall of the next, so that the heat from the combustion gases is used to preheat the bricks in the chambers ahead of the fire. In the same way, the heat from the cooling bricks is used to preheat the air for combustion. In some cases, this combustion air is drawn off by blowers and passed through the grates or burners; in other cases, the fuel, usually in the form of fine coal, is introduced through ports directly into the chambers under fire.

This type of kiln has been used to a very small extent for refractories in this country, but abroad, where economy of fuel is more important, the compartment kiln has been extensively employed. The main trouble with the older type of chamber kiln was the slow rate of fire travel, which amounted to only about 6 in. per hr. This was due mainly to the considerable resistance to the flow of gases through the long passages. In the more modern chamber kilns, blowers and suction fans are being used to

increase the gas velocity, which gives a fire travel as high as 3 to 5 ft per hr, with an immense increase in the capacity of a given kiln.

In a well-designed chamber kiln, practically the only heat loss is by transfer through the walls and crown, for nearly all the heat is abstracted from the cooling bricks and from the combustion gases. Although it is difficult to get strictly comparable figures, it may be said that the fuel consumption runs between one-half and one-third of that of a periodic kiln. This, of course, is an important saving. However, the initial cost for chamber kilns is somewhat higher than for periodic kilns of the same capacity; and in general, the firing of a chamber kiln requires more skill to produce an evenly burned product. In regard to the upkeep of the chamber kiln, different operators hold rather conflicting views, but some believe it to be considerably higher than for a periodic kiln.

TABLE 45. FUEL CONSUMPTION OF CHAMBER KILNS

Ware	Fuel	Maximum temperature		Fuel per M standard bricks, lb
		°F	°C	
Fireclay	Coal	2450	1340	750
	Coal	2325	1273	1,000
	Coal	2570	1410	1,100
	Producer gas	2590	1420	1,500 (coal)
Silica	Coal	2640	1450	900
Magnesite	Coal	2680	1470	1,500
	Coal	3000	1650	3,500
	Brown coal	2730	1500	4,000

The capacity of chamber kilns depends entirely upon the size and number of chambers, as well as rate of fire travel. Kilns with an output of over 100,000 bricks per day have been constructed.

During the Second World War the Didier Werke in Germany constructed a Hoffman-type chamber kiln[13] with three kiln cars per chamber, so that the setting could be carried out in the open. Such a kiln should receive serious consideration by our manufacturers for burning shapes.

5. Tunnel Kilns. The use of tunnel kilns in burning refractories is extending rapidly, and it may be said that practically all the modern refractory plant units are built around a tunnel kiln. As the design has been improved and experience gained in the operation of tunnel kilns, it is generally recognized that they will produce better bricks at a lower cost than the periodic-kiln unit. This does not mean that the periodic kiln

will not be used, for it still offers advantages in burning large or intricate shapes, where the burning schedule must be different from that of the standard brick. Because of the great importance of the tunnel kiln, some space will be devoted to a consideration of the principles of operation.

In principle, the tunnel kiln consists of an elongated chamber, which is maintained at a steady temperature, graded in the desired manner, from end to end. The charge, mounted on cars, is moved continuously through the chamber and encounters in its passage the desired variations in heat. The economy of the tunnel kiln is obtained by regaining the heat from the combustion gases to heat the incoming charge and by using the heat from the cooling bricks to preheat the combustion air or, in some cases, to dry the bricks.

The advantages of the tunnel kiln are as follows:

1. The tunnel kiln lends itself well to a continuous production process, which minimizes handling.

2. The setting and drawing of the kiln are simple and regular; and with dry-pressed brick, setting can be done directly from the press, eliminating the shods, drier cars, etc.

3. The kiln structure itself, with the exception of the cars, is always at a uniform temperature, so with proper design, upkeep of the refractory of the kiln itself is very low.

4. It is possible by proper design to heat and cool the ware according to any desired schedule, which enables the brick to be burned properly in the shortest possible time.

5. Owing to the relatively small cross section of the charge, the heat is able to penetrate to the center rapidly, thus allowing much more rapid burning than is possible in the bulky charge of the periodic kiln. This rapid burning is an advantage when special orders must be put through rapidly.

6. The tunnel kiln, when properly operated, shows marked economy of fuel in comparison with the periodic kiln.

There are a number of disadvantages to the tunnel kiln, but many of these are gradually being eliminated as more experience is gained with this method of burning.

1. The construction of a tunnel kiln necessitates a considerable capital outlay, as it is impossible to increase the capacity gradually as can be done with a number of periodic kilns. However, the cost per thousand bricks produced is not necessarily higher than that with the periodic kiln.

2. A shutdown on a tunnel kiln is serious, as it will tie up the whole unit for perhaps two to four weeks. With proper operation, a shutdown is very rare, but it does happen occasionally.

3. The upkeep on the car tops is high, because of the fact that they are periodically heated and cooled during each passage through the kiln. Considerable study is being given the problem, and it seems probable that this expense can be greatly reduced by careful design.

4. Some difficulty is experienced in getting a uniform temperature across the section of the tunnel kiln. The top and sides of the charge are often hotter than the bottom. This can be corrected, however, for some tunnel kilns now running give a very uniform temperature distribution.

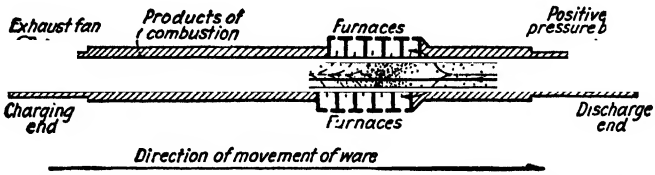


FIG. 138. A plan section of a direct-fired tunnel kiln. (*American Refractories Institute.*)

5. The tunnel kiln requires a considerable length of floor space, and some plants are so situated that this is not readily available.

6. Another objection to the tunnel kiln is that for most efficient operation, it must be run with a uniform charge, *i.e.*, with straight bricks or 9-in. shapes. It is, of course, possible to vary the burning schedule to accommodate larger shapes or different types of clay, but these changes have a bad effect on the structure of the kiln, and some time is lost in getting the kiln running uniformly after such a change is made.

7. The tunnel kiln cannot be run efficiently at a low capacity and therefore lacks the flexibility of the periodic kiln.

Tunnel kilns are made in the direct-fired and muffle types. Because the average refractory is not very sensitive to impurities in the atmosphere, the muffle type, which is more expensive in first cost and in fuel, would rarely be selected for burning refractories; therefore we shall confine ourselves to the direct-fired type. In Fig. 138 is shown a plan section of a typical direct-fired tunnel kiln. The charge enters the kiln at the left-hand end and is gradually heated, reaching a maximum temperature in the hot zone. It is then cooled as it passes out of the kiln. Cold air is forced into the exit end of the kiln with a blower, and this passes through the charge, cooling it and at the same time picking up heat. This air then passes into the combustion zone, where it is mixed with the combustion gases, and then passes through the incoming charge. In this portion of the kiln, it loses heat to the charge; then it is drawn out at the entrance end of the kiln with a suction fan. The primary air used for combustion in the burners is usually drawn out from the cooling section by a fan, but this is small in volume compared with the total gas flow.

A number of variations may be used. In Fig. 139 the cooling air is drawn out of the kiln and used for heating driers or a hot floor, and the air for combustion is taken from the cooling air at the same point. Figure 140 shows a kiln with indirect cooling. In this case, the bricks are cooled

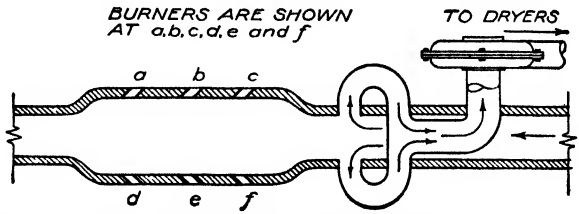


FIG. 139. Tunnel kiln in which the cooling air is drawn out for use in drier.

entirely by radiation, as the cooling air passes through the hollow walls and is used for driers and combustion.

In order to regulate the heating curve of the bricks, the gases are usually not drawn off at one point at the kiln entrance but are taken out at a number of points along the preheating section so that the desired temperature curve may be obtained.

The longer the preheating zone of the kiln the cooler will be the exit gases and the higher the efficiency of the kiln. However, for constructional reasons, the length must be limited; consequently the temperature of the exit gases usually runs between 100°C (about 212°F) and 400°C (about 750°F). In the same way, the outgoing bricks may be cooled to any desired temperature by sufficient length of the cooling zone. It is generally desired to cool the charge sufficiently for easy handling. The bricks usually emerge at temperatures of 50°C (about 120°F) to 150°C (about 300°F).

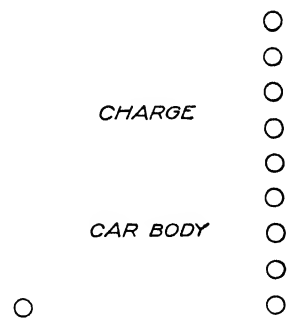


FIG. 140. A tunnel kiln with indirect cooling.

The setting of the charge itself should be so proportioned that a comparatively high gas velocity is maintained throughout the length of the preheating zone, and yet excessive power should not be required to pull the desired volume of gases through. In general, the velocity of the gases through the preheating zone will vary from 500 to 2,000 ft per min, and the draft at the entrance end needed to supply this velocity will vary from ¼ to 1 in. of water.

A great many methods are used in setting the charge to provide

longitudinal gas channels. As the sides of the charge have a tendency to heat before the center, it is common practice to provide a gas channel down the center of the charge and to reduce the clearance at the top and sides to a minimum, as shown in Fig. 141. The width of the charge usually ranges from 4 to 7 ft, and the height from 4 to 6 ft. Rather flat arches are used in order to prevent gas from flowing over the charge. It is quite necessary in a kiln of this length to make the sections as airtight as possible. This is accomplished by keeping the wall joints well cemented;

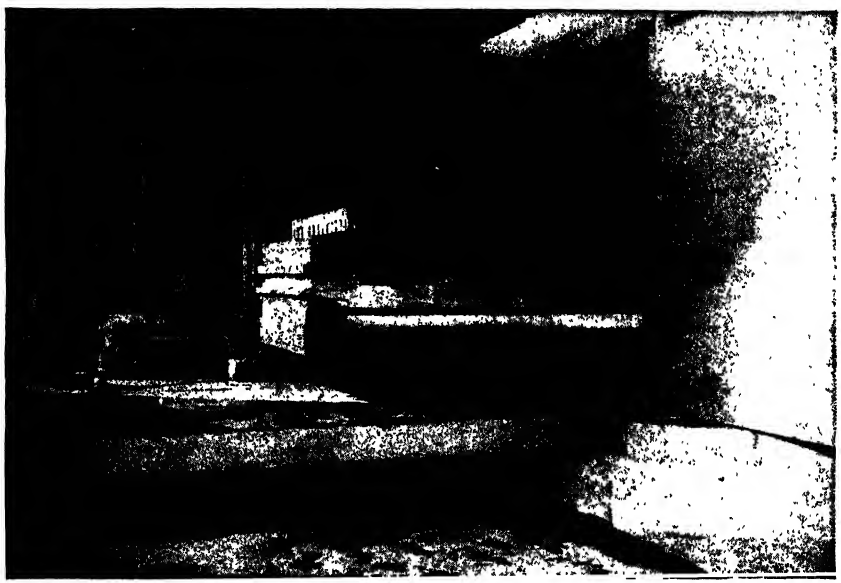


FIG. 141. A car of chrome bricks being pulled from the tunnel kiln onto a transfer car. (*Courtesy of the Harbison-Walker Refractories Company.*)

and in some cases, airtight coatings are applied to the outside of the insulating material.

There would tend to be a very large leakage between the car bottom and the kiln wall, because the clearance here cannot be made small on account of the change in dimensions of the car top. This leakage is prevented in most kilns by attaching to each car a blade that runs in a trough filled with sand along each side of the kiln, as shown in Fig. 142. This method appears to be quite satisfactory, as sand can be supplied to the entrance end of the trough from which it is gradually carried through to the exit end, where it can be removed and returned.

The furnaces for firing tunnel kilns are arranged along the sides in the firing zone as shown in Fig. 143. The number of furnaces usually varies

between two and seven on each side, and usually they are staggered. For the use of coal, furnaces and grates similar to those used in periodic kilns are employed; but in this case, they may be designed to work at their maximum efficiency with a constant load. Although a number of kilns have been fired directly with coal, in general it is more difficult to maintain a uniform temperature, and better control is obtained with other fuels. Many tunnel kilns are fired with oil. In most cases, the burners are placed in small chambers at the side of the firing zone, and the oil flame is directed into the charge. Due to the necessarily small distance between the burner and the charge, there is danger of overheating the surface of the brick next to the burner. For this reason, a checkerwork, as shown in Fig. 130, is sometimes placed at the mouth of the chamber to distribute the heat more evenly over the surface of the charge.

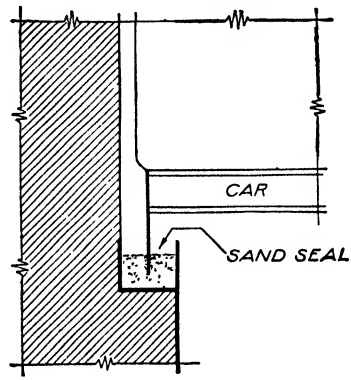


FIG. 142. A sand seal under a tunnel kiln car.

Kilns fired with natural gas need only a small firing chamber, as the flame is comparatively short. As in the case of periodic kilns, natural

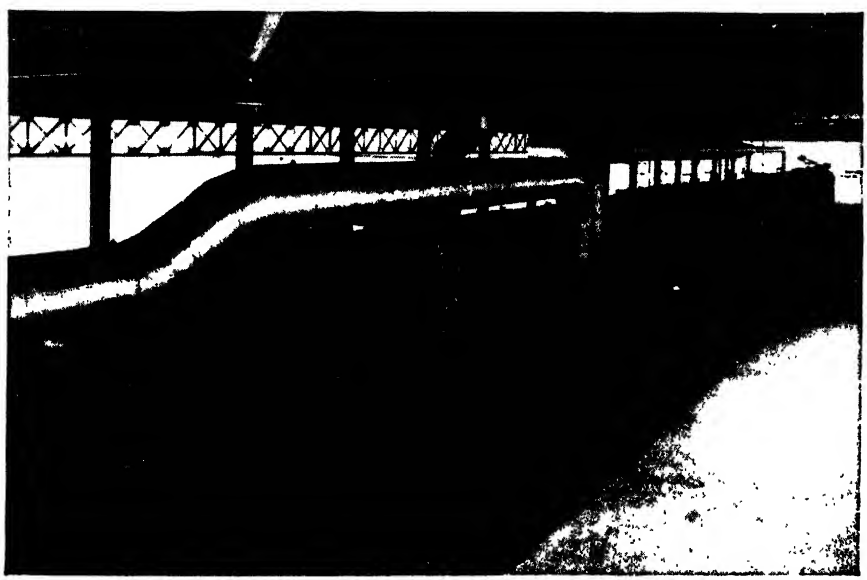


FIG. 143. A modern tunnel kiln designed for firing refractories. (*Courtesy of the Allied Engineering Corporation.*)

gas is an ideal fuel, and perfect control of temperature and atmosphere can be maintained with it.

Producer gas is often used in firing tunnel kilns. In most cases, the flame can be directed immediately into the charge because of the low temperature of the producer-gas flame. Because of the low heat value of this gas, it is not necessary to use a large amount of secondary air to provide a sufficient volume of gases to carry the heat down the kiln. As previously stated, raw producer gas has the disadvantage of depositing soot and tar in the connecting flues, and provision must be made for cleaning them out periodically.

The position of the burners is usually somewhat below the center of the charge in order to bring up the bottom temperature, which tends to lag behind that of the top. Sometimes burners in the hot zone are varied in height from one point to another in order to give a more equal temperature distribution to the charge. Some kilns have been constructed with hollow car bottoms. In this case, the car tops must be made of excellent material to withstand the high temperatures and loads experienced under these conditions.

The tunnel kiln cars vary from 5 to 7 ft in length and are built of structural steel or made of castings. Generally the cars roll on wheels mounted on roller bearings as in track cars. The track, however, is laid with great care, and there is little side clearance between the flanges and the rails. A number of other methods have been suggested and tried out for supporting the cars, such as balls running in grooves, floats on a canal, and stationary rollers in the kiln.

The cars are pushed through the kiln generally by a hydraulic pusher operated by a small variable stroke pump, as shown in Fig. 144. After one car has been pushed in, the plunger draws back, a second car is inserted by means of a cross transfer, and the process is repeated. At the exit end, the car is taken off on a transfer in the same way. Kilns have been built where the cars are moved continuously rather than intermittently, in which case, they are usually driven by a heavy chain with dogs. Means are provided to transfer the load gradually from the driving dog on the forward car to that on the following car to prevent shock and jars. As it is more expensive to construct a mechanism for continuous operation, it is not generally used, because the wait of four or five minutes while changing cars is not serious.

Nearly all tunnel kilns employ air locks at both ends so that the flow conditions in the kiln will not be disturbed by the entrance or exit of cars. However, kilns can be run with one lock and, in the smaller sizes, without any.

The cars are moved at the rate of from 3 to 8 ft per hr, depending upon the length of kiln and the burning properties of the clay, thus giving a total time in the kiln of from 50 to 100 hr; however, kilns are operating successfully at speeds as high as 20 ft per hr and with a total time in the kiln of 12 hr. If the kiln is properly designed so that the combustion gases are evenly distributed around each brick, the limit in rate of heating for many clays is the time taken for the heat to penetrate from the surface to the center of the brick. In the future, we may see clay refractories burned in a much shorter time than is considered possible at present.

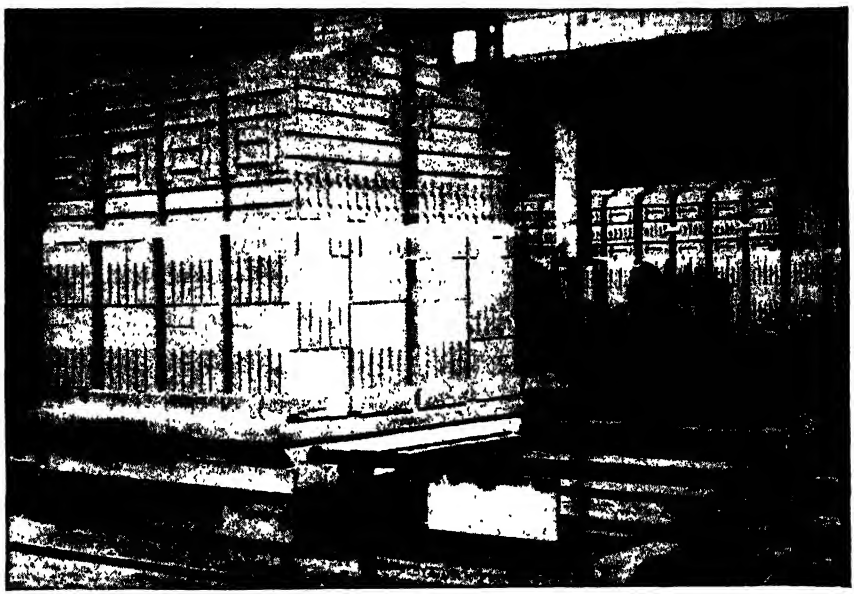


FIG. 144. A tunnel kiln car loaded with special shapes ready to enter the kiln. (*Courtesy of the Harbison-Walker Refractories Company.*)

The production of tunnel kilns generally used for refractories varies between 20,000 and 35,000 bricks per day. It may be said that the faster the bricks can be run through a given kiln and still be burned properly the more efficient will be the burning conditions. It takes but little more fuel to burn 30,000 bricks per day in a given kiln than it does 20,000 bricks.

Some manufacturers burn all shapes in their tunnel kilns, even up to 45 in. in length. They also change the burning temperature to accommodate different types of clay that may be run through the kiln. Although this procedure can undoubtedly be followed if necessary, a tunnel kiln

can be run efficiently only with one type of setting and one temperature adjustment. Any changes in the setting or in the temperature disturb the balance of the kiln and require a long period for readjustment. Again, if the kiln is running slowly enough to burn large shapes properly, it is running slower than necessary to burn standard bricks. Probably the most desirable condition would be to have one tunnel kiln running on 9-in. sizes and a second kiln on a slower schedule burning only large shapes.

A well-designed tunnel kiln will use from one-half to one-third of the fuel per thousand bricks required for a periodic kiln. In Table 46 are given some figures on the fuel consumption of tunnel kilns.

TABLE 46. THE FUEL CONSUMPTION OF TUNNEL KILNS

Type of refractory fired	Fuel used	Maximum temperature		Fuel per 1,000 bricks
		°C.	°F.	
Fireclay	Coal	1270	2320	700 lb.
		1335	2435	900 lb.
		1470	2680	1,250 lb. (stokers)
Fireclay	Oil	1400	2550	80 gal.
		1670	3040	150 gal.
Fireclay	Producer gas	1150	2100	850 lb. (coal)
		1250	2280	970 lb. (coal)
		1420	2590	1,150 lb. (coal)
		1400	2552	630 lb. (coal)
Fireclay	Natural gas	1140	2080	6,000 cu. ft.
		1100	2000	7,000 cu. ft.
Chrome	Oil	1470	2680	500 gal.
		1525	2775	600 gal.

A tunnel kiln reduces the setting and handling cost in a unit by as much as 20 to 35 per cent, through the continuous flow of materials. In the case of dry-pressed bricks, it is general practice to set the tunnel-kiln cars directly from the dry press and then to pass them either through a drier or, in some cases, directly to the kiln. This eliminates drier cars, shods, and storage space for the drying bricks.

It is difficult to state definitely the relative qualities of a tunnel-kiln and a periodic-kiln product because the conditions are so varied. It may be said in general, however, that the tunnel-kiln product is more uniform than that of the periodic kiln, both as to size and as to degree of burning. This is due to a more even temperature in the small cross section of the tunnel kiln and to the fact that the stresses resulting from the height of

the setting and the shrinking of the charge as a whole are much smaller in the tunnel kiln. Kiln marking is rarely found. The tunnel-kiln product is probably no better than the best of the periodic charge, but a large portion of the charge from the periodic kiln will undoubtedly be inferior to any of the tunnel-kiln product.

The cost of building a tunnel kiln to burn refractories will run about $3,000 to $5,000 per thousand bricks per day. This cost takes in only the kiln itself, and a complete unit for manufacturing 30,000 clay bricks per day would cost in the neighborhood of $300,000 to $400,000.

Undoubtedly, a modern tunnel-kiln unit can turn out bricks at a lower cost than the old periodic unit, because of both the saving of fuel and the saving of labor. This fact and the general belief that the product is superior to the periodic product have led many manufacturers to change over their plants to tunnel-kiln operation.

Tunnel kilns are used successfully to fire refractories other than fireclay. Silica bricks have been burned in tunnel kilns here and abroad for some time. A kiln for burning silica bricks at the rate of 35,000 bricks per day would be approximately 500 ft long to give a comparatively long soak at the maximum temperature, which would run around 1500°C (about 2730°F). Magnesite and chrome bricks are being successfully burned in tunnel kilns. These bricks are not able to support a great load while they are being burned; and in periodic kilns, it is necessary to support them more or less completely with silica bricks. In a tunnel kiln, however, the setting can be made so low that the bricks are well supported during the burning operation, which gives a lower kiln loss and a superior product.

6. Shaft Kilns. Shaft kilns are used to a considerable extent in burning lime, dolomite, and magnesite, although they have been displaced by the rotary kiln in many instances.

Shaft kilns for burning magnesite are described by Seil.[13] The coal-fired kiln is 6.5 ft in diameter and 40 ft high. The fuel weighs 35 per cent of the clinker. A blast pressure of 1 lb is used, which produces a temperature at the base of the stack of 1500°C (about 2730°F) and 250°C (about 480°F) at the top. The lower lining is magnesite brick, and the remainder firebrick. The producer gas-fired kilns are 8 ft in diameter and 52 ft high.

A small shaft kiln is described by C. L. Norton, Jr.,[75] for firing pebbles. At a temperature of 1650°C (about 3000°F) only 1000 Btu was required per pound of product—a very high efficiency for such a small kiln. The maximum temperature attainable in this type of kiln is mainly limited by the refractories.

7. Rotary Kilns. Rotary kilns are coming into extensive use in the refractories industry[13] for firing hard-burned grog of fireclay, bauxite, or diaspore. These kilns are similar in construction to those used in the

Portland cement industry and so need no detailed description. Lump clay is fed into the cool end of the kiln and is fired up to temperatures of around 1650°C (about 3000°F). Considerable experience is needed in operating these kilns at high temperatures to prevent rings forming in the hot zone and so stop the flow of clinker.

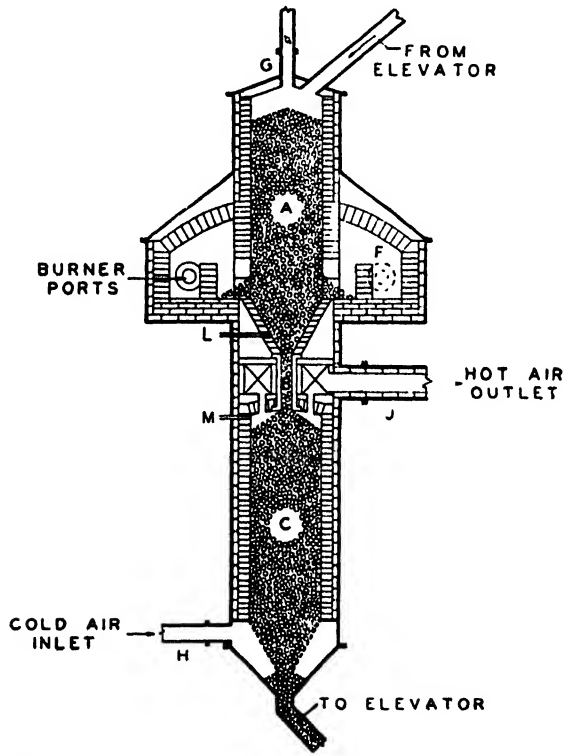


FIG. 145. Arrangement of pebble heater for delivery of air at 2300°F.

8. Air Preheaters. Considerable advances have been made during the last few years in developing high-temperature preheaters to supply combustion air. The most interesting design is the pebble heater,[75] a section of which is shown in Fig. 145. The pebbles ($\frac{5}{16}$-in. spheres of refractory) are heated in the upper bed *A* by burners *F* and flow by gravity through the throat *B* into the lower bed *C*, where air is blown through them to pick up the preheat. The cooled pebbles are then returned to the upper bed by a continuous conveyor. Preheat temperatures of 1370°C (about 2500°F) can be obtained in this very compact device. Actual operating data on a small unit is given in Table 47.

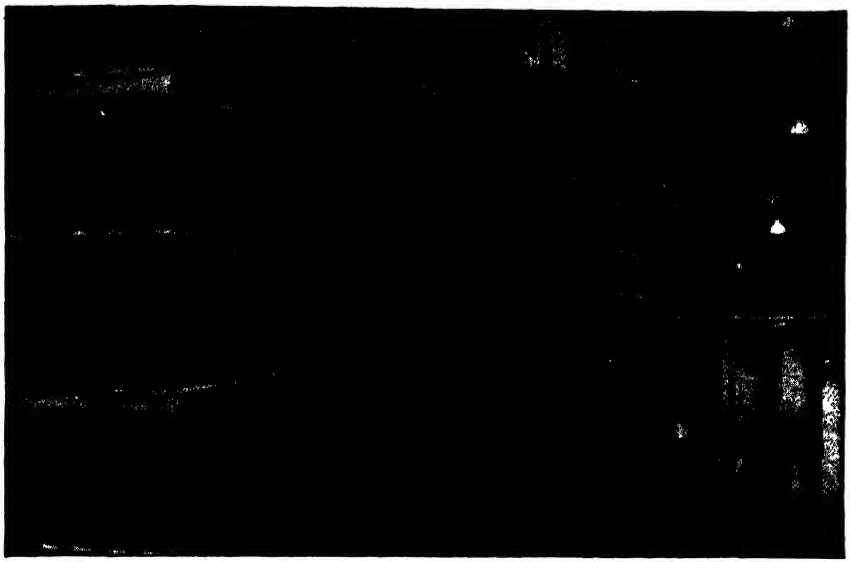


FIG. 146. Showing a modern method of storing fire brick on pallets with a lift truck. (*Courtesy of the Harbison-Walker Refractories Company.*)

TABLE 47. TYPICAL PEBBLE HEATER OPERATING DATA*

	Unit No. 1
Gas being heated	Air
Exit gas temperature, °F	2,180
Inlet gas temperature, °F	100
Weight of gas heated, lb per hr	1,800
Btu per hr in fuel	1,760,000
Weight of flue gas, lb per hr	2,240
Pebble circulation, lb per hr	2,150
Flue gas exit temperature, °F	750
Lower bed diameter, in.	19

* Computed.

9. Handling and Storage. Products from the kiln are either shipped or put in storage directly. In recent years, nearly every plant employs lift trucks and wooden pallets for handling as shown in Fig. 146. This allows high piling with a minimum of labor. In some cases, the bricks are loaded in the freight cars on the pallets, which are later returned when a carload accumulates.

Insulating firebricks are generally ground to sizes on automatic grinders and then packed in cartons for storage or shipment.

CHAPTER X

LABORATORY KILNS AND FURNACES

1. Combustion Furnaces. *Types of Gas Burners.* There are a number of types of burners suitable for the efficient combustion of gas. The simplest is the atmospheric type, where the primary air is drawn in by the gas jet. Examples of this are the Bunsen, Tirrill, and Meker type of burner, as shown in Fig. 147. With gas at the usual pressure of 3 to 6 in. of water,

FIG. 147. The Bunsen, Meker, and Tirrill types of atmospheric gas burners. (*Courtesy of Eimer and Amend.*)

it is impossible to draw in enough primary air for complete combustion; consequently a certain amount of secondary air must be supplied in addition. With natural gas, which requires a larger proportion of air, the primary air is quite insufficient for combustion; therefore it is much more difficult to design an efficient burner of this type to burn natural gas. However, by proper design, furnace temperatures as high as 1420°C (about 2590°F) can be obtained with atmospheric burners without preheating the air. If the air is preheated, temperatures as high as 1750°C (about 3180°F) can be obtained. The advantages of the atmospheric type of burner are quietness and reliability, for a burner of this type can be left running unattended quite safely.

Although it is possible to preheat the air for small kilns successfully, fuel saving is usually not an object in such small installations, and the initial cost and maintenance of a suitable recuperator is not often justified; accordingly, when temperatures above the range of the atmospheric burner are desired, it is best to use the air or gas under pressure. By supplying the gas at a comparatively high pressure with a small pump, sufficient primary air can be drawn in to give complete combustion. Under the

conditions of complete combustion at the top of the burner, a much higher temperature can be obtained than when secondary air must be supplied separately. The high-pressure-gas type of burner has the advantage of a very large range of control from the lowest to the highest temperatures. The greatest disadvantage is the special apparatus that must be used for compressing the gas.

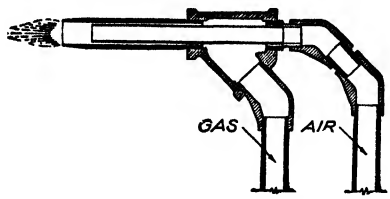


FIG. 148. A blow pipe where the gas and air are mixed at the nozzle.

Perhaps the most common types of gas burners used in laboratory kilns are the ones to which the air is supplied under pressures of from 2 to 12 psi. The gas and air are mixed at the nozzle somewhat as shown in Fig. 148, and a fairly short flame results. Temperatures as high as 1800°C (about 3270°F) can be obtained with this type of burner. In controlling the heat of the furnace, two adjustments must be made—one on the gas and one on the air—but this has the advantage of allowing the kiln atmosphere to be regulated as desired.

The highest temperatures in laboratory kilns can probably be obtained by premixing the gas and air in the theoretically correct proportions and then burning them at the nozzle, as shown in Fig. 149. Under proper conditions, temperatures up to 1850°C (about 3360°F) can be obtained without preheating. The high temperature is due to the fact that the gas and air are intimately mixed before combustion and that the combustion itself occurs extremely rapidly in a very small volume.

FIG. 149. A gas burner in which the air and gas are premixed and then burned at the nozzle. (*Courtesy of the Maxon Premix Burner Company.*)

Small Round Kiln for Shrinkage Tests, etc. Figure 150 shows a furnace that is very convenient for heating small specimens. By placing the specimens in open saggers, a very even temperature is attained because of the complete circulation of the gases around the specimens. The use of premixed air and gas gives temperatures up to 1800°C (about 3270°F).

High-temperature Catenary Kiln. In Fig. 151 is shown a small kiln that has proved very successful in firing refractory specimens up to 1850°C (about 3360°F) with city gas and no preheat. Excellent results

were obtained with a lining of pure, fused alumina bricks insulated with kaolin insulating firebrick. The insulation is omitted for a short distance at the door end of the arch, both to keep this spot from overheating and to equalize the temperature over the whole kiln. When firing, the temperature is brought up to about 1500°C (about 2700°F) overnight with a

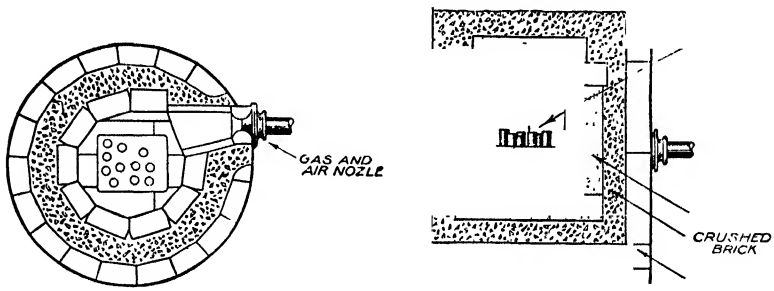


FIG. 150. A gas furnace for temperatures up to 1800°C.

blow pipe, the premix is started in the morning, and 1800°C (about 3270°F) reached in 5 hr.

Large Laboratory Kiln. Shown in Fig. 152 is a drawing of a laboratory kiln of sufficient size to burn 100 to 500 standard-size bricks. This size of kiln is very convenient for making burns on experimental bricks or special shapes, where the schedule is different from that of the production kilns. The kiln can be fired by either gas or oil, and temperatures up to 1750°C (about 3180°F) can be obtained. The temperature distribution

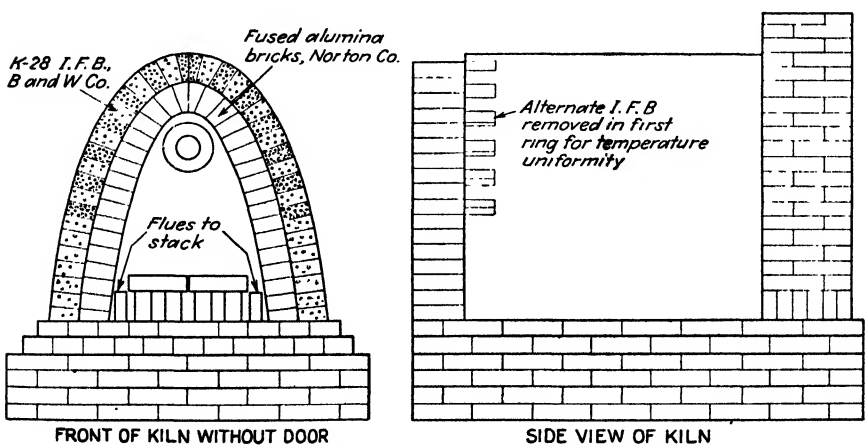


FIG. 151. High-temperature catenary kiln for the laboratory.

can be made quite uniform by varying the floor openings. It will be noted that the elimination of the side walls on this kiln greatly simplifies the construction and makes it unnecessary to use much ironwork.

Oxygen-propane Furnace. The furnace shown in Fig. 153 is used for firing special refractories up to 2000°C (about 3630°F) with a lining of

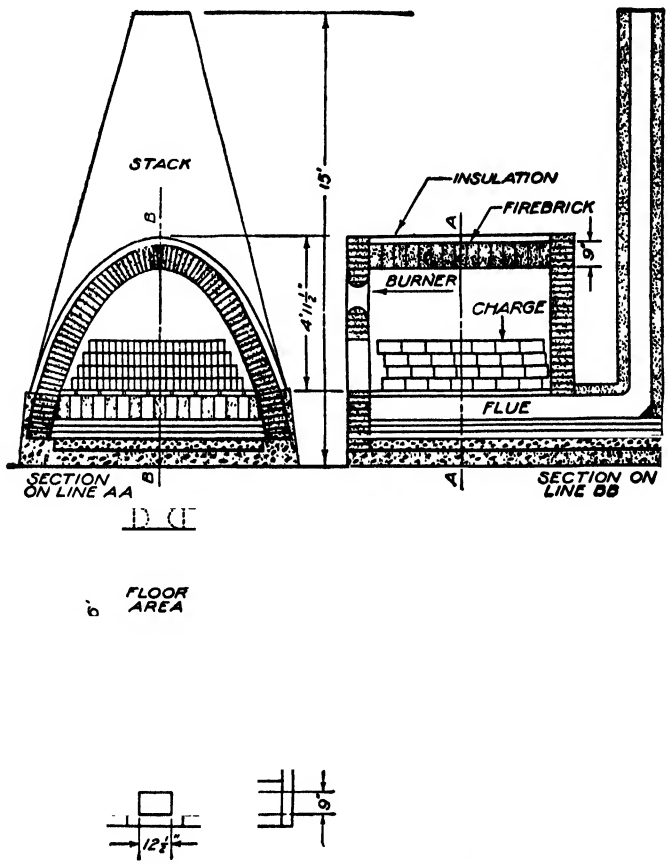


FIG. 152. A laboratory kiln for burning 100 to 500 bricks.

pure fused alumina bricks, which stand up well although there is some melting on the inner surface of the bricks at the highest temperatures. While this furnace is more expensive to run than gas and air furnaces, it reaches high temperatures rapidly and the gas velocity in the furnace is not very high. The temperature uniformity in the furnace is not perfect, and therefore specimens should not be placed in line with the burners. With the use of a zirconia lining, still higher temperatures are possible.[4]

2. Electric Resistance Furnaces. *Globar Kiln.* The kiln shown in Fig. 154 is excellent for firing up to 1500°C (about 2730°F), as the temperature and atmosphere can be positively controlled. Also the uniformity of temperature is excellent, as there is a circulation of the gases up around the heating elements and down through the ware. This kiln may be made up in various sizes but a suitable variable voltage power supply is needed. Kilns of this type may be purchased on the market.

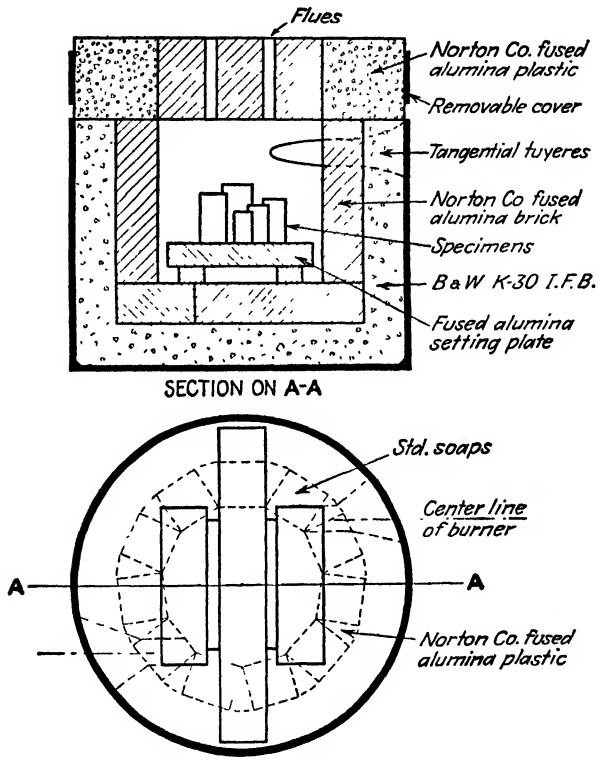


FIG. 153. A small oxygen-propane furnace.

Carbon Tube Furnace. This furnace has been much used in high-temperature research; but as it is rapidly being superseded by high-frequency induction furnaces, it need not be discussed further.

Oxide Resistor Furnace. This furnace developed at the National Bureau of Standards[9] using resistors of the Nernst type is capable of reaching 2000°C (about 3630°F). This is the only high-temperature electric furnace capable of providing an oxidizing firing, and therefore is valuable for research in spite of its high cost.

3. Arc Furnaces. For extremely high temperatures the arc furnace has been used. The high temperature is concentrated into a small volume of ionized gas heated by the current passing through it; therefore it is difficult to obtain a uniform temperature over a reasonably large volume for research purposes.

4. Solar Furnaces. This type of furnace[5,6] produces very high temperatures of 3000°C (about 5430°F) by focusing the image of the sun onto a specimen. Some of the melting points of the more refractory substances have been determined in this way, as quick heating and freedom from contaminating gases are achieved. However, the operation is completely dependent on the weather.

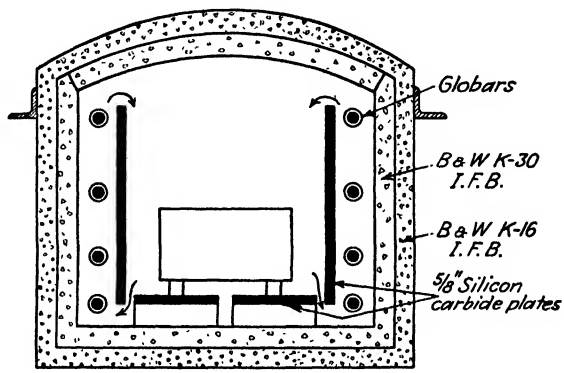


FIG. 154. Globar kiln.

5. High-frequency Induction Heating. *Introduction.* It is believed that high-frequency induction heating will be the principal tool of high-temperature research in the future; therefore considerable space will be devoted to this subject.

In 1831, Michael Faraday described an experiment in which two coils of wire were wound on an iron ring, thus making the first transformer on record. This experiment was the first realization of the phenomenon of electromagnetic induction. Shortly after 1850, a large number of patents were issued, both in the United States and abroad, covering high-frequency apparatus for the heating of metals. General interest and the use at that time were for melting, wherein a conducting crucible was heated by induction and the heat of the crucible was transmitted to the charge by radiation and conduction. Today, this same principle, in conjunction with various modifications, is finding wide application in the refractory research field due to the ease in obtaining extremely high temperatures in various atmospheric conditions. Because there seems to be a real lack of specific information to guide the research worker in designing

equipment for extreme temperature levels, the following section gives the general principles as well as four practical designs.

Prior to the entry of the United States into the Second World War, a large part of all high-frequency heating in the refractory research and other fields was accomplished with experimental or custom-built high-frequency generators. However, the requirements of diversified experimentation and production opened new market possibilities, until now there is available a wide range of high-frequency heating equipment in standard commercial models. Practically all these models are applicable, in one way or another, to the refractory research field. In addition, custom-built units are available from nearly all manufacturers of standard models to meet special requirements.

The application of high-frequency heating in the refractory research field divides into two distinct groups: (1) induction heating units for the direct heating of electrically conductive materials (susceptors) and (2) dielectric heating units for the direct heating of electrically nonconductive materials. Since few data are available regarding the dielectric heating of refractory materials to high temperatures, we shall not consider this method in the following discussion. On the other hand, a considerable amount of data is available in regard to the induction heating of susceptors, which, in turn, are used to heat enclosed refractory materials to high temperatures through thermal radiation and conduction phenomena. Applications of this method will be our only concern here.

Principles of Induction Heating. We are interested fundamentally in raising the temperature of the susceptor by transformation of electromagnetic energy to heat energy. The only requirement that a material must have in order that it be capable of responding to induction energy and thereby become heated is that it be an electrical conductor. Materials with properties suitable for susceptors in high-temperature work are listed in Table 48, and reaction temperatures in Table 49. It should be noted that many materials such as glass conduct electricity at elevated temperatures. If, for instance, glass is brought up to an elevated temperature by conventional means, further increase in temperature can be obtained by high-frequency induction-heating methods. The same may hold for some oxide mixtures such as 80 per cent ThO_2, 10 per cent Y_2O_3, 10 per cent ZrO_2; 90 per cent ThO_2, 10 per cent Y_2O_3; and 85 per cent ZrO_2, 15 per cent Y_2O_3, which are good conductors at high temperatures.[10] However, the problem of raising them to a conducting temperature has not been worked out but would be of great importance in providing a means for high-temperature heating in air.

An induction heating circuit is fundamentally a transformer wherein an inductor carrying the high-frequency alternating current from the

generator is the primary and the susceptor to be heated is made the secondary by merely placing it within the confines of the inductor, there being no physical contact between the two. The current flowing through the inductor sets up magnetic lines of force in a circular pattern, which

TABLE 48. PROPERTIES OF SUSCEPTOR MATERIALS

Material	Symbol	Melting point., °C	Elec. res., micro ohms per cm	Vapor pressure, mm Hg	Rate of volatilization, g per sq cm per sec
Carbon (graphite)	C	3500	1,000	10^{-2} at 3000°C[22]	
Molybdenum	Mo	2620	5.7	10^{-3} at 2300°C[23]	
				6.43×10^{-9} at 1800°C[22]	8.63×10^{-11} at 1800°C[22]
				3.96×10^{-5} at 2200°C[22]	4.80×10^{-7} at 2200°C[22]
				1.60×10^{-2} at 2600°C[22]	1.79×10^{-4} at 2600°C[22]
Platinum	Pt	1774	9.83	Below 10^{-4} at 1700°C[23]	
Tantalum	Ta	2850	15.5	Between W and Mo, near W[4]	
Tungsten	W	3370	5.51	6.45×10^{-12} at 2000°C[22]	1.14×10^{-13} at 2000°C[22]
				4.92×10^{-8} at 2400°C[22]	7.98×10^{-10} at 2400°C[22]
				2.86×10^{-6} at 2800°C[22]	4.29×10^{-7} at 2800°C[22]
				3.33×10^{-3} at 3200°C[22]	4.67×10^{-5} at 3200°C[22]
Columbium*	Cb	1950	20		
Iridium*	Ir	2350	6.08		
Osmium*	Os	2700	9		
Rhenium*	Re	3000	21		
Rhodium*	Rh	1985	4.93		
Titanium*	Ti	1800	3		
Vanadium*	V	1710	26		
Zirconium*	Zr	1900	41		
Carbides†					
Nitrides†					
Sulfides†					

* For possible future use.
† Few data available.

TABLE 49. REACTION TEMPERATURES IN DEGREES CENTIGRADE FOR SOME PURE MATERIALS IN A VACUUM*

	W	Mo	MgO	BeO	ThO_2	ZrO_2	C
W							
Mo	2300						
MgO	2000	1800					
BeO	2100	1900	1800				
ThO_2	2300	2200	2150	2150			
ZrO_2	2100	2150	1950	2000	2200		
C	1500	1600	1800	2300	1950	1800	

* From Doctor's Thesis by P.D. Johnson, Massachusetts Institute of Technology, 1948.

thread through the susceptor and induce eddy currents therein. Since the high-temperature susceptor materials mentioned are nonmagnetic, heating caused by hysteresis can be ignored, but the eddy-current phenomenon is of primary importance.

Eddy-current losses are resistance losses resulting from small circulating currents within the material. These currents are caused to flow by virtue of differences in potential at various points in the material, these differences in potential being caused by the alternating magnetic field threading through the susceptor. This loss, or heating effect, is proportional to the square of the current flowing and directly proportional to the electrical resistance of the susceptor. Hence, it can be considered to be proportional to the square of the frequency and the field strength, since the potential differences and resulting currents vary in accordance with this relation.

A characteristic of high-frequency heating is its tendency to concentrate energy on the surface of the susceptor. This phenomenon, called "skin effect," is a function of frequency. Other factors being equal, the higher the frequency the shallower will be the depth of penetration of the heat zone.

Close coupling between the inductor and susceptor is important and deserves due consideration. The curve in Fig. 155 shows the increase in over-all efficiency of the inductive combination as the coupling is varied from 0 to 1. A coupling of 0 means that the diameter of the inductor is infinitely greater than the diameter of the susceptor; the coupling of 1 (theoretical) means that the inductor is wound tight on the susceptor. In addition, the coupling should be made as close as possible because of the economic advantage of obtaining the highest possible power factor as measured at the inductor terminals. The higher the power factor the less the cost of correcting it with static condensers to give the desired unity power factor at the generator terminals.

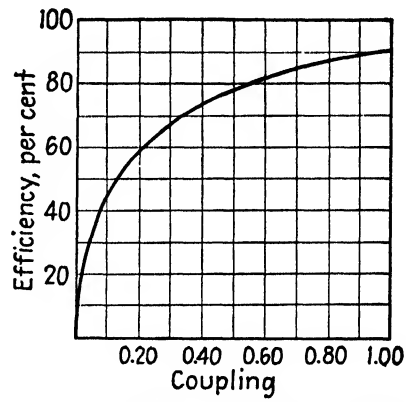


FIG. 155. Effect of coupling on heating efficiency.

Inductors are generally made of high-conductivity copper tubing. The inductor may be made of a single turn of copper or more, depending upon the size and shape of the susceptor and the inductive balance needed to obtain efficiency for the specific purposes. Vaughan and Williamson[14] have worked out many useful data pertaining to the design of inductors for use with nonmagnetic susceptors. We have found that units designed

by means of their equations have final characteristics very close to the desired values, and it is recommended that their work be followed closely in any new design.

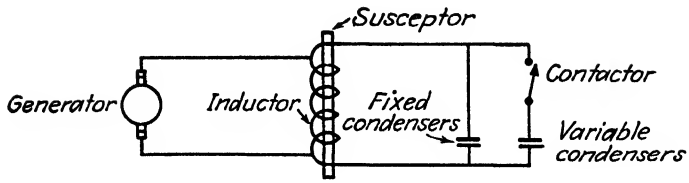
High-frequency Generators for Induction Heating. Four different types of equipment are in common use: (1) rotating machines (see Fig. 156*A*) producing frequencies of 1 to 10 kc per sec and power outputs of 7.5 to 1,500 kw, (2) mercury-arc frequency converters (see Fig. 156*B*) producing frequencies of 0.50 to 80 kc per sec and power outputs of 2 to 600 kw, (3) spark-gap converters (see Fig. 156*C*) producing frequencies of 100 to 500 kc per sec and power outputs of 2.8 to 500 kw, and (4) vacuum-tube oscillators (see Fig. 156*D*) producing frequencies of 100 to 915,000 kc per sec and power outputs of 0.6 to 200 kw. Unfortunately, available technical data on commercial units cannot always be correlated on a comparable basis.

No single rule can be applied to determine which of the various commercial-model high-frequency generators may be suitable for a specific purpose. In general, it may be said that the rotating-machine types offer comparatively good power regulation in the low range independent of the maximum power output rating of the machine. For this reason this type is very good for slow heating, which is advisable with low-thermal-conductivity materials such as refractories. For heating small, thin susceptors, the vacuum-tube types are sometimes preferred. Much can be said about the simplicity of design and low maintenance of the mercury-arc and spark-gap types. Usually direct consultation with any of the manufacturers listed in Table 50 or others, outlining specifically the problems to be met by the generating equipment, is advisable to assure that the costs be kept to a minimum and that the installation operates satisfactorily.

Specific Applications. In review, the methods used in heating refractory materials by means of high-frequency generators employ high-melting-point, electrical-conducting materials as susceptors. In all cases, the susceptor is made to surround the refractory body to be fired. The choice of a generator having the proper characteristics will afford the particular rate and efficiency of heating of the susceptor.

Since some refractories and most susceptor materials react with air at elevated temperatures, firing in high vacuum or special atmospheres usually becomes necessary. These methods along with the ordinary air firing are discussed in detail below.

Furnace for Firing at Atmospheric Pressure. Graphite is used for the susceptor in this furnace. Usually a strong reducing atmosphere is present, but various gases such as nitrogen, hydrogen, helium, and argon can be continuously flushed through the system to vary the conditions. Temperatures up to 3000°C (about 5430°F) have been reached without undue



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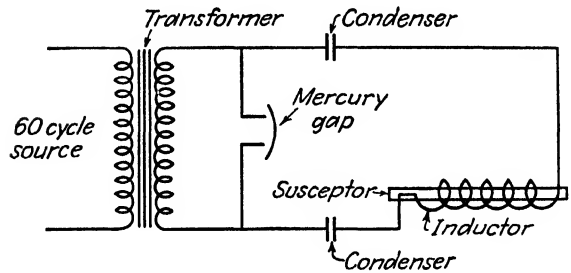

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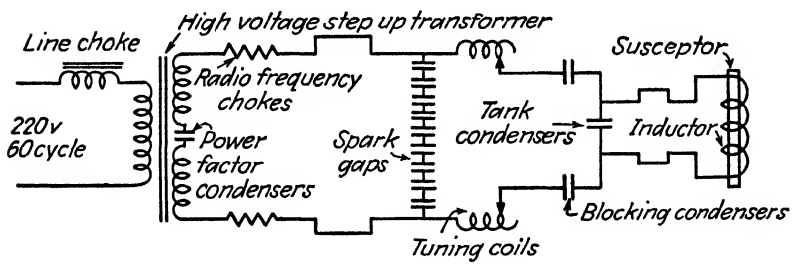

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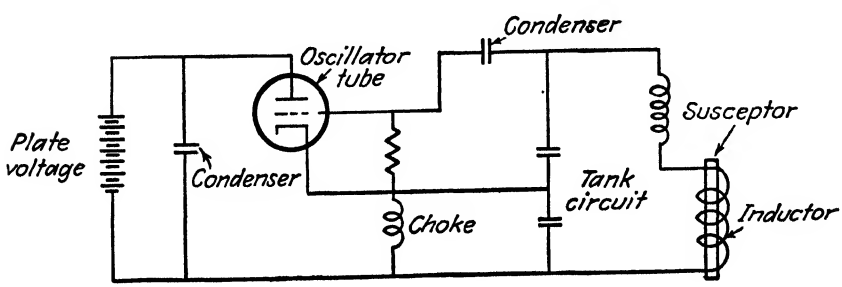


D

FIG. 156. The four principal types of high-frequency generators.

difficulty. In order to fire refractories in this system, care must be taken to prevent reaction of the graphite with the refractory material in question. Under ordinary conditions graphite will react with various refractories at the temperatures shown in Table 49. The temperatures are not too precise but may be used as helpful guides.

TABLE 50. COMMERCIALLY AVAILABLE HIGH-FREQUENCY GENERATORS FOR INDUCTION HEATING (1948)

Manufacturer	Type of generator	Power output range, kw	Frequency range, kc
Ajax Electrothermic Corp., Trenton, N.J.	Mercury arc	2–30	10–80
	Rotating machine	50–1,200	1–10
Allis-Chalmers Mfg. Co., Milwaukee, Wis.	Mercury arc	300 600	0.5–1.5
	Vacuum tube	20–100	400–500
Budd Induction Heating Corp., Detroit, Michigan	Vacuum tube	20	500
	Rotating machine	50–900	3–10
Ecco High Frequency Corp., North Bergen, N.J.	Spark gap	About 3–30	100–500
	Vacuum tube	5–50	100–30,000
	Rotating machine	20–1,250	3–9.6
General Electric Corp., Schenectady, N.Y.	Vacuum tube	5–50	530–915,000
Illinois Tool Works, Chicago, Ill.	Vacuum tube	0.5–50	2,000–6,650
Induction Heating Corp., New York, N.Y.	Vacuum tube	5–25	375–20,000
Lepel High Frequency Laboratories, New York, N.Y.	Spark gap	2.8–21	150–400
	Vacuum tube	1	400
Ohio Crankshaft Co., Tocco Division, Cleveland, Ohio	Rotating machine	7.5–200	3–9.6
	Vacuum tube	0.75–20	450–3,000
Radio Corp. of America, RCA Victor Division, Camden, N.J.	Vacuum tube	1–75	400
Scientific Electric Div. of "S" Corrugated Quenched Gap Co., Garfield, N.J.	Vacuum tube	0.6–150	200–1,500
Westinghouse Electric Corp., East Pittsburgh, Pa.	Vacuum tube	5–200	200–400
	Rotating machine	20–1,500	0.96–10

Since the reaction temperature and rate of reaction between the graphite and the refractory material are a function of degree of contact, many ingenious methods have been devised to obtain higher firing temperatures than are shown in Table 49. For instance, coarse refractory grog can be placed between the graphite and the refractory body to decrease the degree

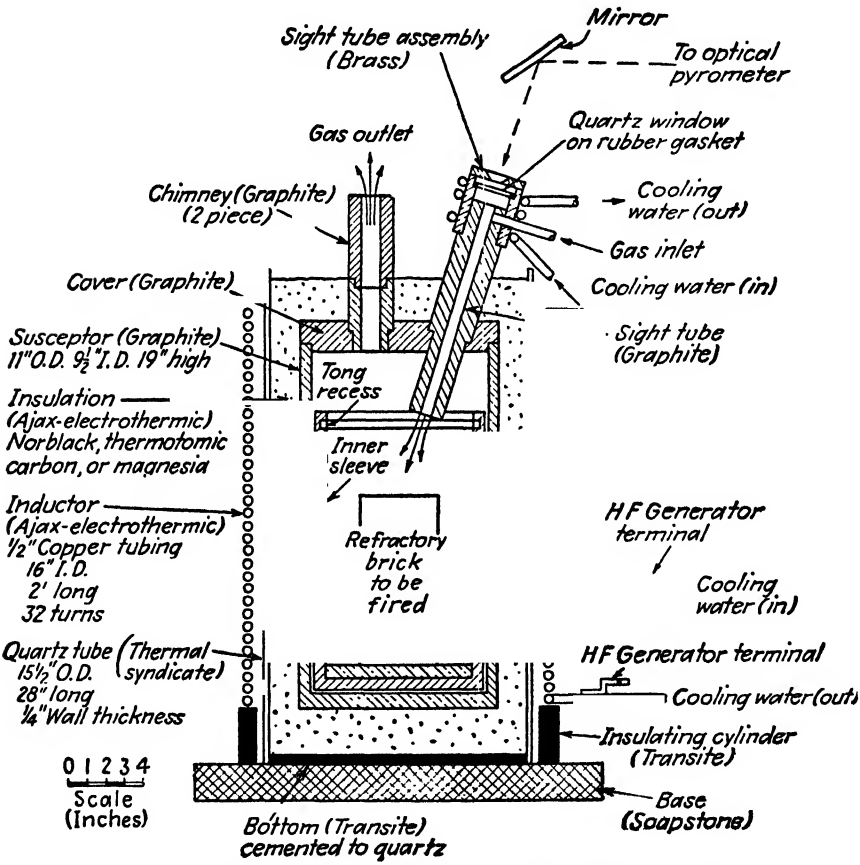


FIG. 157. High-frequency furnace for firing at atmospheric pressure.

of contact. In some instances, (one or more) plates made of the refractory body material or dissimilar materials can be used to separate the graphite from the refractory body; the plate or plates, in many cases, will react but will not affect the refractory body if the time at temperature is not excessive. As can be seen from Fig. 157 the furnace construction is simple. The major components are as follows:

High-frequency generator (Ajax Electrothermic Corp.) 30 kw output, mercury-arc type

Inductor, 16 in. i.d., 24 in. long, 32 turns (standard design, Ajax Electrothermic Corp.)

Silica tube, 15 in. o.d., 14 in. i.d., 28 in. long (Thermal Syndicate); a transite disk may be cemented to the bottom of the tube to retain the finely divided carbon

Insulation, Therm-atomic carbon or Norblack (Ajax Electrothermic Corp.); any other finely divided carbon material or magnesia could be used

Susceptor, graphite (National Carbon Co.)

Sight tube fitting, brass, custom built

Inner sleeve, graphite (National Carbon Co.)

The graphite parts are easily machined from the commercially available bars or billets. The chimney can be made in two parts as shown; the joint should be coated with finely divided carbon to reduce the heat loss due to thermal conductivity, and this can be also done in the case of the graphite sight tube. The water-cooled sight tube head is of simple construction, and a small flow of helium or nitrogen will clear the sight tube of fumes, and hence, accurate optical pyrometer measurements can be obtained. The inner furnace sleeve is removable by means of the tong groove shown, and the finely divided carbon can be extracted by means of a vacuum cleaner.

Table 51 lists data obtained in a typical firing for a standard-size refractory brick to be heated to 2000°C (about 3630°F) in 180 min and held at 2000°C (about 3630°F) for 30 min.

TABLE 51. FIRING CYCLE IN ATMOSPHERIC-TYPE FURNACE

Time, min	Output of generator, kw	Temperature, °C
0	13	
30	13	
60	27	
90	27	975
120	27	1350
150	27	1700
180	27	2000
210	18	2000
Furnace off		

Vacuum-firing Systems: General. As was mentioned previously, it may be deemed desirable to fire refractory bodies in high vacuum or controlled atmospheres. In the majority of instances, due to the affinity of the susceptor materials toward oxygen and other gases at elevated

temperatures, the use of high-vacuum or controlled-atmosphere techniques is an absolute necessity.

It has been found that closed systems designed for high-temperature vacuum-firing can readily be used for heating refractory bodies to high temperatures in other gaseous atmospheres at pressures below 1 atm. The following discussion will therefore be limited to the understanding of some of the general design principles utilized in building high-temperature vacuum-firing systems. Three types of such equipment have been found useful and will be described in detail. All types afford vacuums better than 10^{-5} mm Hg if designed and handled properly. In designing any one of these systems, care must be taken to choose not only the most efficient high-frequency generator and allied components but also the proper fore pump, diffusion pump, valves, duct sizes, gages, and other equipment.

In general, a high-vacuum system is a sealed system in which the firing or vacuum chamber is connected by ducts to a diffusion pump in series with a mechanical fore pump. A large portion of the molecules of gas (usually air) in the firing chamber are sucked out of the system by means of the mechanical fore pump. The mechanical fore pump is usually capable of holding a vacuum pressure of 0.10 mm of Hg. In order to obtain a higher vacuum and faster pumping rate, a diffusion pump is placed between the firing chamber and the fore pump. A good percentage of the remaining molecules are literally dragged out of the firing chamber owing to the operating principle of the diffusion pump. Operating principles concerning diffusion pumps are discussed in detail by Strong.[17] The molecules in all cases are exhausted from the fore pump to the atmosphere.

Under ordinary atmospheric conditions (760 mm Hg, 20°C) 1 cc of gas contains about 2.5×10^{19} molecules. If this volume is evacuated to 10^{-6} mm Hg, only 3.3×10^{10} molecules remain. As may be seen from the above figures, all but 1/1,000,000,000 of the original number of molecules are absent. The following may further clarify the concept of high vacuum.

The mean free path of a molecule is the average distance traveled by the molecule before collision by another and may be expressed for a single gas by the following equation:

$$\lambda =$$

where λ = the mean free path, cm
n = the number of molecules per cc
d = the molecular diameter, cm

Since the molecular diameter of nitrogen is 3.1×10^{-8} cm, the mean

free paths (at 0°C, found from the above equation) at various pressures are shown in Table 52.

TABLE 52. MEAN FREE PATH OF NITROGEN GAS MOLECULES FOR AMBIENT PRESSURES

Pressure, mm Hg	Mean Free Path, Cm
760	8.5×10^{-6}
1	0.0065
10^{-3}	6.5
10^{-4}	65
10^{-5}	650
10^{-6}	6500
10^{-9}	6,500,000

A better understanding of the physical properties of gases may be obtained from the following equations:

$$n = 0.49\ \rho v_{av} \lambda$$
$$k = \eta C_v \epsilon$$

where n = the viscosity coefficient, g/sec/cm
k = the thermal conductivity, cal/sec/cm/°C
ρ = the gas density, g/cc
c_v = the heat capacity at constant volume of 1g of gas
ϵ = a constant, 2.5 for monatomic gases, and 1.9 for diatomic gases
v_{av} = $(2.1 \times 10^8 T)/M$ cm/sec = average velocity of the molecules where T is the absolute temperature and M the molecular weight of the gas

It has been found experimentally, somewhat contrary to and therefore limiting the use of the previous equations, that viscosity n decreases quite appreciably at pressures below 0.10 mm, and the thermal conductivity k of a gas essentially disappears below 10^{-4} mm.

Table 53 compares the molecular diameters, viscosity, and thermal conductivity coefficients for five gases commonly used at standard temperature and pressure.

TABLE 53. PHYSICAL PROPERTIES OF VARIOUS GASES

Gas	Molecular diameter d, cm	Coefficient of viscosity n, g per sec per cm	Thermal conductivity k, cal per sec per cm °C
Hydrogen..	2.47×10^{-8}	86×10^{-6}	318×10^{-6}
Nitrogen...	3.50×10^{-8}	166×10^{-6}	52×10^{-6}
Oxygen....	3.39×10^{-8}	187×10^{-6}	56×10^{-6}
Helium....	2.18×10^{-8}	189×10^{-6}	339×10^{-6}
Argon.....	3.36×10^{-8}	210×10^{-6}	39×10^{-6}

Mechanical Pumps. The ordinary single-stage or compound reciprocating type of mechanical pumps are extremely efficient units at atmospheric pressures but are of little value by themselves if high vacuums are required. Vane-type rotary pumps have been used successfully at pressures below 10 mm Hg, but with appreciable loss in efficiency. Better vacuums can be obtained by using a diffusion pump in series with the reciprocating- or vane-type rotary pumps. On the other hand, eccentric cylinder-type precision high-vacuum pumps, available in single-stage and compound types, maintain their pumping efficiency well below 1 mm Hg. As can be seen from the curve in Fig. 158*A* high pumping speed is not retained at the lower pressure regions. An excellent description of these pumps is given by Sullivan.[21a]

Diffusion Pumps. By placing a mercury or oil diffusion pump in series with a mechanical pump not only are larger effective pumping speeds made possible (even at high pressures), as shown in Fig. 158*B*, but ultimate pressures of 10^{-7} mm or better can be obtained, providing a cold trap is employed to reduce the effective partial pressure of the mercury or the oil.

Pumping speeds for ideal diffusion pumps may be roughly calculated from the following equation:

$$\frac{dv}{dt} = A\sqrt{1.32 \times 10^7 \frac{T}{M}} \text{ cc/sec}$$

where dv/dt = the volume of gas escaping through the area of aperture A, per unit of time
A = the area of aperture
M = the molecular weight of gas = 29 for air at room temperature (T = 300°K)

Therefore the value of dv/dt at room temperature is

11,700 cc/sec = 11.7 liters/sec for an aperture of unit area A

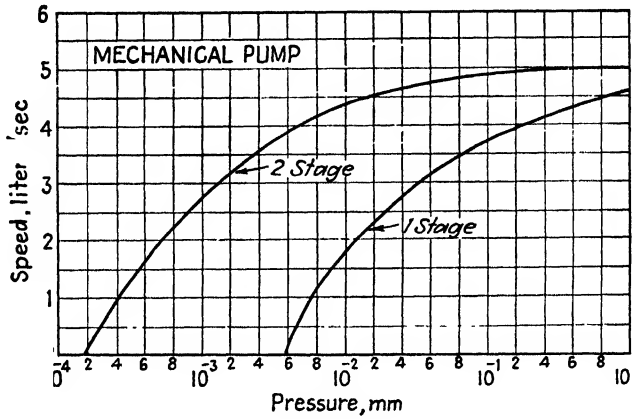
Since area A should be considered a hypothetical aperture unit area and if a perfect vacuum is obtained in the chamber, then a perfect pump would have a speed of 11.7 liters per sec. The speed of a diffusion pump is expressed as the volume of gas passing through the throat of the pump at the pressure measured at the throat. The speed factor of a pump is

$$\frac{\text{Speed per unit area of throat}}{\text{11.7 liters/sec}}$$

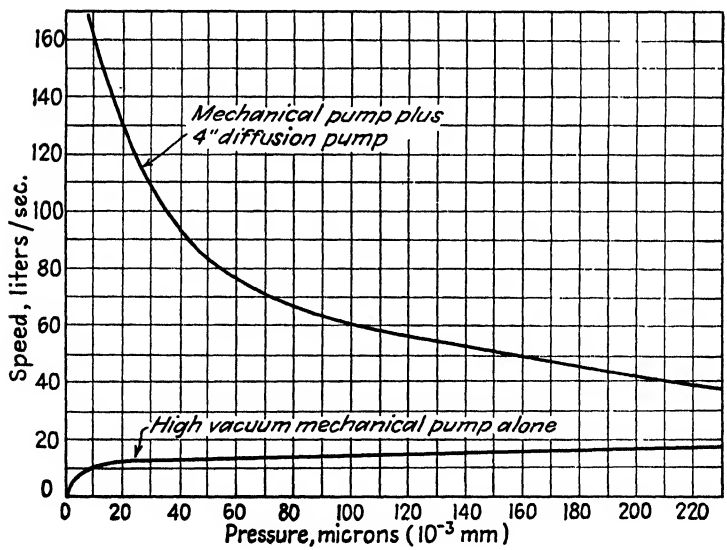
Oil diffusion pump values approaching 0.6 have been obtained. On the other hand, mercury pump speed factors are relatively lower, approaching 0.3 generally. The use of mercury as a boiler fluid in the diffusion pump in all cases necessitates the use of a cold trap in the system owing to the

high vapor pressure of the mercury. This is discussed by Blears and Hill.[21b]

A fore pressure of less than 0.50 mm Hg created by the mechanical pump is usually required for efficient operation of the diffusion pump. The



(A)



(B)

FIG. 158. Mechanical and diffusion pump characteristics.

curve in Fig. 158*B* shows the effect of adding a diffusion pump in series with a mechanical pump for evacuating a closed system. The maximum pressure in the fore line against which a pump will maintain its speed is important in

most applications. While this is primarily a function of pump design, it is also dependent on the type of oil used and the amount of heat actually delivered to the oil. The trend between various boiler fluids used in diffusion pumps is for the higher vapor pressure oils to work against the higher fore pressure.

Stability of pump oils can be considered as stability against oxidation when hot and resistance to thermal dissociation in the diffusion pump boilers caused by excessive intensity of heating at the heater and boiler fluid interface. The resistance to oxidation is very high in the case of the silicones and at least equal to that for the chlorinated hydrocarbons. This resistance is, in fact, sufficiently high to make possible distillation at atmospheric pressure as a means for reconditioning the oil.

TABLE 54. RELATIVE MERIT OF DIFFUSION PUMP BOILER FLUIDS[20]
1 Being Best

Type oil	With liquid air trap, all pressures	Without cold trap		Pump fore pressure requirements	Stability to air	Stability to heat
		Greater than 5×10^{-5}	Less than 5×10^{-5}			
Silicone (high boiling)	3	2	1	3	2	2
Typical ester	3	2	2	3	4	3
Straight hydrocarbon	3	2	2	3	3	2
Chlorinated aromatic hydrocarbon	2	1	3	2	2	2
Mercury	1			1	1	1

Selection of the best oil for a particular application must be made carefully. Where extremely high vacua are required, silicones give the best performance because their boiling points can be adjusted as required and consequently low vapor pressure can be secured. In addition, the stability remains excellent. In the range of intermediate vacua created by diffusion pumps, all the oils are reasonably satisfactory. Where good speed and exceptional fore-pressure characteristics are required at a sacrifice in ultimate vacuum, the higher vapor pressure compounds remain superior. Table 54 offers an estimate of the relative merits of various oils as applied to vacuum-pumping conditions normally encountered. Listing is in order of apparent merit, 1 being best. No exact values are given because of the uncertainty in the absolute meaning.

Duct Design. No matter how good the vacuum at the pump, it is evident that the pressure in the vacuum or firing chamber may be excessively high if the piping and connections are not designed to handle the flow of gas with an economically low pressure loss due to friction. Flow

of gases at low pressures may be described as streamlined flow, slip flow, or molecular flow. Under conditions where the mean free path of the gas molecule is comparable to the diameter of the duct, the gas flow impedance, or "resistance," will vary linearly with the duct length and inversely as the cube of the diameter of the duct. It is desirable to avoid elbows or bends in the ducts; where necessary smooth bends as opposed to sharp bends tend to minimize frictional losses. At very high pressure, the flow of gas in a duct can be calculated by the conventional means. In the intermediate range of pressures (1 to 100 μ) a more complex relationship exists between pumping speed and pressure. Excellent data on the flow of gases in round ducts at low pressures are available from the work of Brown, DiNaido, Cheng, and Sherwood.[21]

Gages for Measurement of Low Pressure. Pressure is usually expressed in millimeters of mercury by the high-vacuum worker. A pressure of 1 mm thus corresponds to the pressure exerted by a column of mercury 1 mm in height. The term micron (μ) is sometimes used; 1 micron = 10^{-3} mm Hg. Table 55 should tend to establish the working limits of the various types of gages in use today.

TABLE 55. VACUUM GAGE TYPES[19]

Type of gage	Useful range of pressure, mm Hg	
	Low limit	High limit
Mercury manometer	1.0	760 and above
Oil manometer	0.01	10
McLeod gage	10^{-5}	10
Pirani gage	10^{-4}	2.0
Thermocouple gage	10^{-4}	2.0
Viscosity gage	10^{-5}	10^{-3}
Knudsen gage	10^{-5}	10^{-3}
Ionization gage	10^{-8}	10^{-3}

The conventional mercury U-tube manometer serves as an excellent instrument for the measurement of pressures in the millimeter range. By substituting low-vapor-pressure oils for mercury, a considerable increase in sensitivity can be achieved because of their lower inherent densities.

The McLeod gage has for many years been generally employed for the measurement of low pressures. With this instrument a known volume of gas, the pressure of which is to be measured, is compressed in a capillary tube, and the resulting pressure read in terms of a mercury column. Although such an instrument is not continuous reading, its calibration can be determined from its physical dimensions, and such an instrument thus serves as an excellent primary standard for the laboratory.

The Pirani and thermocouple type are the most useful for the reading of pressures in the micron range. Although both must be frequently recalibrated if the highest accuracy is required, instruments of this class give continuous readings and are physically rugged. The principle of operation in both cases involves the heating of a filament with an electric current. The change in thermal conductivity of the surrounding gas as a function of pressure can then be translated into electrical units in a variety of ways. In the case of the Pirani gage the resistance of the heated filament changes in accordance with the degree of cooling caused by the amount of pressure in the chamber, while the voltage developed by the thermocouple in the thermocouple gage depends on the amount of cooling experienced by the heated filament.

Although a number of ways have been devised for the measurement of the lowest pressures, the ionization gage (with the possible exception of the Knudsen) is the only one now found generally useful. This instrument is essentially a type of three-element radio tube. One of the electrodes serves as an anode, and the resulting electron stream creates positive ions. These ions migrate to the negatively charged "collector," and the resulting current serves as an indication of the pressure within the tube. Although some ionization tubes are capable of operating at pressures above 10^{-3} mm, their usefulness lies in the region below 10^{-5} mm, and even pressure approaching 10^{-9} mm can be determined.

Many problems are involved in the measurement of pressure other than the finding of an instrument capable of reading within the range of interest. A McLeod gage, for example, gives an indication of the pressure exerted by the *gases* in the system on the assumption that Boyle's law is valid at low pressures. Consequently, false readings will be obtained when easily condensable vapors are present. A Pirani, on the other hand, will read the total pressure of the *gases* plus all *volatile* constituents. In the determination of pressures in the region of 10^{-3} mm (and below) such questions as absorption and adsorption of gas and the position of the gage relative to the point in the system at which the pressure is desired must be also considered.

Glass, Vacuum, High-frequency Furnace. The all-glass system shown in Fig. 159 is by far the best for heating small refractory pieces in experimental work when vacua of 10^{-5} and better are desired. Temperatures exceeding 2600°C (about 4710°F) have been reported in this type of system in conjunction with a 10-kw thermonic vacuum-tube-type high-frequency generator. The firing chamber is usually made of clear quartz for high-temperature work, but Vycor or Pyrex glass can be substituted when long-continued runs at temperature are not required.

As can be seen in Fig. 159*A*, the top of the quartz firing chamber is sealed with a ⅛ in. thick, optically flat, clear quartz plate through which

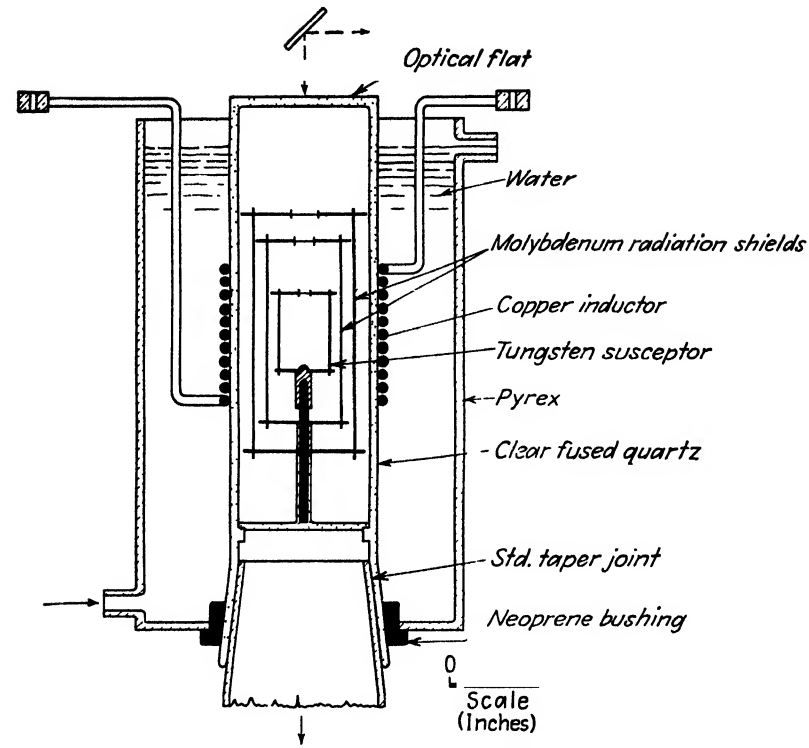


FIG. 159. A glass, vacuum, high-frequency furnace.

optical pyrometer readings are readily obtained. A standard $^{45}/_{50}$ standard taper full-length quartz joint is fused to the lower end of the firing chamber. A matching $^{45}/_{50}$ standard taper full-length Pyrex joint (male) is fused to the ducting, which leads to a cold trap and glass diffusion pump. The cold trap is made of Pyrex and is used to condense the vapors coming from the firing chamber so that they will not contaminate the diffusion pump boiler fluid. If mercury is used for the diffusion pump fluid, the cold trap is absolutely necessary due to the high vapor pressure of mercury. In this system the two-stage diffusion pump, model GF-20A made by Distillation Products, Inc., Rochester, New York, uses 125 g of Octoil as the boiler fluid. The rated pumping speed of this pump is 20 liters per sec at 10^{-4} mm; the ultimate vacuum obtainable is 7×10^{-7} mm Hg.

The metal fore pump used to back the diffusion pump can be of any model capable of maintaining a fore pressure of 0.03 mm at a pumping speed of 0.5 liters per sec. If necessary, a smaller diffusion pump can be inserted between the main diffusion pump and the fore pump to guarantee the required fore pressure at the main diffusion pump.

The susceptor and reflectors are made of tungsten and molybdenum in this particular case, but other materials such as are mentioned in Table 48 can be substituted. It should be noted that the reflector must be extremely clean in order that the thermal radiation energy from the susceptor be reflected with highest efficiency. As may be seen from Fig. 159*A* the metal parts are supported on a molybdenum rod; this rod is, in turn, supported by a glass or quartz tripod mount. The entire assembly is supported on three concave shelves, which are fused to the quartz tube. The reflectors are not continuous cylinders, as might be thought from the drawing, but, on the other hand, are cut longitudinally to prevent their heating. Normally, a conducting cylinder in a changing magnetic field would be heated inductively; but since the flow of current is perpendicular to the lines of flux, a break in the circuit will prevent the eddy current heating from occurring. All reflectors used in induction heating, therefore, should be fabricated with radial or transverse cuts to prevent this flow of eddy currents. On the other hand if the frequency is too high even the cut shields will heat.

The inductor in this system is of unique design (suggested by Dr. L. S. Foster) in that it is made of solid copper wire and not hollow tubing as is used generally. The entire firing chamber including the inductor and quartz-Pyrex joint assembly is cooled by means of a water manifold made of glass as shown. It should be noted that all standard ground joints should be lubricated with silicone or other stopcock lubricant.

An ionization gage, inserted on the firing chamber side of the cold trap, is used to determine the pressures in the range between 10^{-3} and 10^{-7} mm

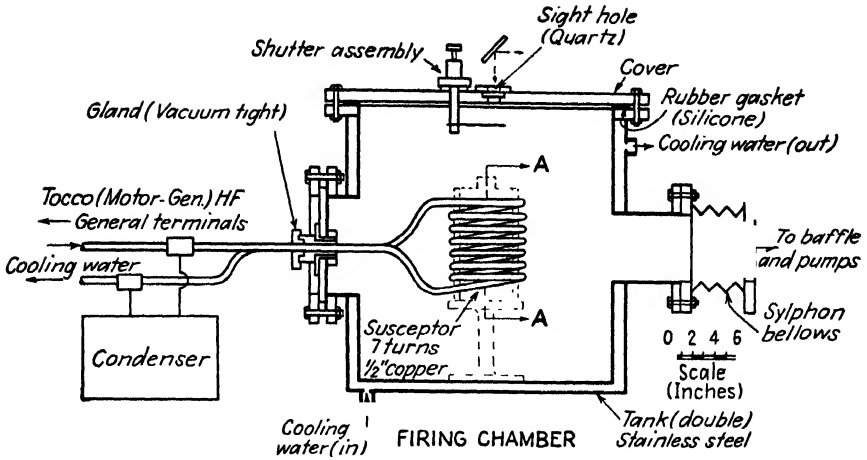
Hg. A mercury manometer is connected to the system at the position shown in order to ascertain roughly the over-all pressure in the system down to 1 mm Hg. Of course, other gages such as the oil manometer, McLeod, Pirani, or thermocouple types could be added to cover the complete pressure range if required.

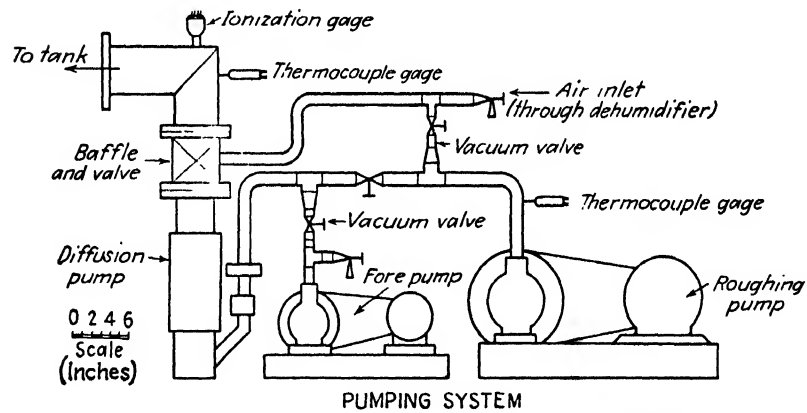
The components are more easily disassembled and cleaned than with the all metal or glass-metal systems. The all-glass system also allows the observation of the interior of the vacuum chamber at all times. When small bodies are to be fired at high temperatures in various gaseous atmospheres, this system is also applicable.

Metal, Vacuum, High-frequency Furnace. The system shown in Fig. 160 was assembled and in part manufactured by the National Research Corp., Boston, Massachusetts, with design features as specified by the Watertown Arsenal Laboratories (J. L. Martin, W. H. Titorchook, and L. S. Foster); however, a similar system was developed previously by Prof. I. Amdur at the Massachusetts Institute of Technology. This system eliminates the vacuumtight silica tube, but there is a voltage limitation when the inductor is in a vacuum.

The power source for the inductor is a modified Tocco Junior, 20-kw motor generator set, type 20 STMC10B. The capacitors, originally located in the Tocco housing, were removed and remounted as close to the inductor as possible to reduce power losses sustained in lengthy inductor to condenser leads. It may be mentioned here that this modification could be applied to many of the standard induction generators available today to increase efficiency. The water-cooled inductor consists of 20 ft of ¼-in. standard-weight copper tubing wound into a seven-turn coil, 6 in. i.d. and 8 in. long with leads about 26 in. long. The coil leads entered a chamber through gasketed seals in a Tur-X plate (International Products Corp., Baltimore, Maryland), which, in turn, is gasketed to the vacuum chamber. The vacuum system consists of a cylindrical stainless steel vacuum chamber that is exhausted by means of an oil diffusion pump backed up by a mechanical pump. By means of a butterfly valve and other vacuum-type valves, it is possible to isolate the diffusion pump from the system and to use the mechanical pump for roughing. When the pressure has been reduced to a sufficiently low value (200 μ), the diffusion pump is cut into the system by proper adjustment of the valves. It is thus possible to isolate the diffusion pump without shutting it off, and the chamber is opened to remove specimens.

The vacuum chamber is constructed of stainless steel, consisting of a double-walled, water-cooled cylinder and bottom closed on the top by a large, removable, stainless steel plate, which carries a similar smaller plate.





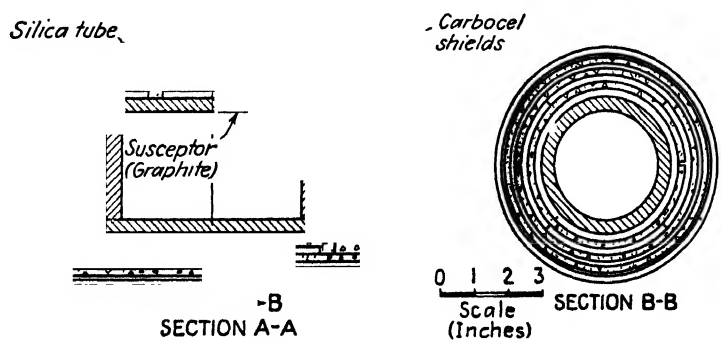


FIG. 160. Metal, vacuum high-frequency furnace.

The chamber is fitted with two diametrically opposed ports: one is used to introduce the inductor leads, and the other carries a flange and sylphon bellows for attachment of the pumping system. Mountings are of a design that permit reorientation of the chamber about its axis so that the chamber can be used not only in the vertical position as shown in Fig. 160 but also horizontally.

The diffusion pump used was a type 104-H6 supplied by the National Research Corporation. This pump has a rated capacity of 1,250 cu ft per min at 2 to 0.5 μ pressure and uses the same manufacturer's "Narcoil No. 10."

The mechanical fore pump is a 25 cu ft per min capacity, size 778, type VSD, Kinney pump and is used in series with the diffusion pump. The pumping time required to obtain the necessary reduction of pressure to 200 μ is about 10 minutes. The National Research Corporation, type 706, thermocouple and ion gage control unit is used to measure vacuum system pressures. The vacuum manifold dry-air pressures are measured by means of a thermocouple gage and an ion gage, and the fore-pressure manifold dry-air pressures are measured by means of a single thermocouple gage. A Bourdon-type vacuum gage is used to indicate approximate pressures when gases such as helium are used to "crack" the vacuum.

The susceptor and its insulation are supported on a refractory table inside the vacuum chamber. The furnace is shown in Fig. 160. Section *BB* is cylindrical and consists of a silica tube, Carbocel components, and graphite susceptor parts. The Carbocel radiation shields are cut longitudinally to prevent heating by induction. A sight hole through the furnace end permits optical pyrometer readings to be made, while a shutter controlled by hand from the outside of the vacuum chamber prevents the quartz window from becoming cloudy owing to vapors condensed within the furnace.

Quartz-metal, Vacuum, High-frequency Furnace. Many systems of this type have been built. The particular system shown in Fig. 161 was built by P. D. Johnson in partial fulfillment of the thesis requirements at the Massachusetts Institute of Technology.

The quartz-metal vacuum-firing system furnace components were designed in the following way. A temperature of 2200°C (about 3990°F) was required for the heating of a cylindrical refractory body 6 in. high and 2 in. in diameter. The rate of heating had to be slow, owing to the poor thermal conductivity of the refractory material. A rotating type of high-frequency generator was chosen because of the excellent control characteristics at low power output afforded by this design. The following machine was used satisfactorily but, of course, was much larger than needed for this furnace: Tocco machine, Ohio Crankshaft Company, type

50PMG10B motor-generator set. Motor, 100 hp, 3 phase, 220 volt, 240 amp, 60 cycle; generator, 50 kw, 220 v, 228 amp, 9,600 cycle. Owing to the size of the refractory cylinder to be fired a susceptor of 2.5 in. diameter by 8 in. high was chosen. Because of the geometry established by the furnace and vacuum chamber, it was decided to use an inductor with a minimum inside diameter of 4.75 in. It was assumed that approximately

FIG. 161. High-frequency induction furnace.

10,000 watts of electrical energy would be necessary from the generator to be transformed into heat energy within the susceptor. The electrical resistance of copper (used for inductor) at room temperature was reported to be about 0.80×10^{-6} ohm inch; for molybdenum (susceptor) the electrical resistance was reported to be 20.0×10^{-6} ohm inch at 2300°C (about 4170°F).

By substitution in the formulas of Vaughan and Williamson,[14] the value for the measure of current penetration in the inductor was found to

be 0.031 in. for good efficiency. The wall thickness of the inductor tubing should be equal to or greater than a factor of 1.35 times the measured current penetration. This value was found to be 0.042 in., so copper tubing with the next largest wall thickness, $\frac{3}{64}$ in., was chosen.

The measure of current penetration or skin effect on the molybdenum susceptor was found to be 0.0142 in. This meant that the susceptor would have to be at least that thick. General availability of molybdenum sheet and other structural factors influenced the final choice of 0.050-in.-thick material.

It was found through the mathematical formulas that the inductor should consist of nine turns. The power dissipated in the transmission lines was taken as zero, since short heavy, high-conductivity copper bus bars were used. From the above data the subsequent substitution in the formulas established the KVA (rated) for the capacitor at 230. As can be seen, the electrical part of the system was designed with all factors known, thus reducing to a minimum the usual trial-and-error experimentation.

The susceptor, then, is made from 0.050-in. sheet molybdenum, while the radiation shields are made of 0.020-in. molybdenum sheet in a continuous spiral. Refractory oxide insulators are used to separate the spiral shield from the exterior horizontal shields, as shown in Fig. 162, and the entire assembly is supported on molybdenum rods. The efficiency of the radiation shields is greatly increased if they have a bright surface; therefore the molybdenum parts should be heated in hydrogen to remove the oxide that is present in commercial sheet.

The vacuum chamber is made of a translucent quartz tube (Thermal Syndicate Corp.). The top of the chamber is closed with the prism assembly using a silicone or neoprene rubber gasket. The shutter, which protects the prism from radiation and from condensable constituents originating in the furnace during firing, is actuated electrically.

Two ports are supplied at the lower vacuum chamber flange; one is used for the manometer gage connection and gas inlet, and the other is used for the ionization gage. A standard 4-in. water-cooled baffle (Distillation Products, Inc.) and a custom-built valve are situated between the vacuum chamber and the pumping system.

The pumping system consists of an oil diffusion pump having a rated pumping speed of 275 liters per sec at 10^{-4} mm Hg pressure (type MC275, Distillation Products, Inc.) and uses Octoil as the boiler fluid. The fore pump has a rated pumping speed of about 6 cu ft per min at 40 μ pressure and is capable of maintaining an ultimate vacuum of 10 μ. The fore pump used is a model VsD556 manufactured by the Kinney Manufacturing Company, Boston, Massachusetts. A thermocouple gage is inserted

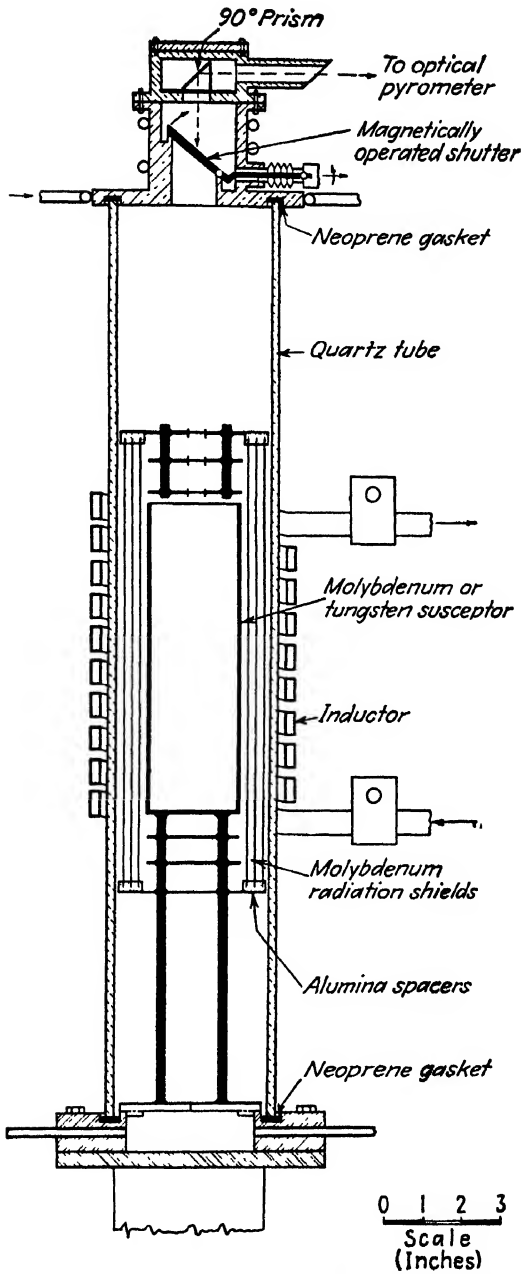


FIG. 162. Quartz-metal, vacuum high-frequency furnace.

between the diffusion pump and the fore pump. In general, the pumping system is similar to the one described for the metal enclosed vacuum-firing system shown in Fig. 160 but is smaller and less complex in design. Typical runs at different power levels for this furnace are shown in Fig. 163.

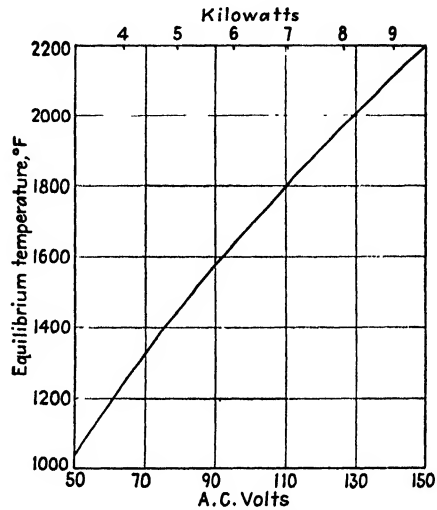


FIG. 163. Performance curves for the quartz-metal vacuum furnace.

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CHAPTER XI

REFRACTORY MORTARS, PLASTICS, CONCRETES, AND COATINGS

1. Introduction. Refractory mortars are used in laying refractory brick and shapes and serve the following purposes: to bond the brickwork into a solid unit so that it will be more resistant to shocks and stresses, to provide a cushion between the slightly irregular surfaces of the brick so that one course of brickwork will have a firm bearing on the course below it, and also to make a wall gastight or to prevent penetration of slag into the joints. The best mortars are combinations of a plastic clay and a volume-constant grog, as the use of raw fireclay alone as a mortar is confined to low-temperature applications.

Mortars are sometimes thinned with water and used as coatings for the face of the refractory walls in order to seal the joints further or to protect the wall from destructive elements in the furnace.

Plastic refractories are used for three general purposes. The first is for making molded refractory shapes to be used in the furnace in the green state; the second is to form a molded monolithic wall or furnace structure; and the third, to repair and patch worn brickwork.

Refractory concretes contain an aggregate and a setting material, such as hydraulic cement, to give them cold-setting properties. The aggregate may be calcined fireclay, which will give a high density to the concrete, or it may be a porous grog, diatomaceous earth, vermiculite, or other porous material to give light weight and low heat conductivity to the resulting concrete.

Hot patching materials are not used very extensively as yet but are intended for forming a stable refractory while the furnace is at operating temperatures.

The general composition of these refractory materials varies a great deal depending upon the application for which they are intended. The majority are made from a fireclay base, but there are many special compositions in which chrome, silicon carbide, silica, and alumina are used. The manufacturer of the brick should be consulted when selecting a mortar or coating.

2. Mortars. *Heat-setting Types.* Mortars in this classification are generally composed of grog and a bond clay. No air-setting ingredient

such as sodium silicate is added, and the mortar obtains its strength by the vitrification of the bond. For low-temperature service or where a strong mortar is needed, a clay high in fluxes should be used for the bond, whereas a mortar for high-temperature service would use a fireclay or kaolin. The nonplastic part is crushed to pass a 40-mesh screen and mixed with the bond. To reduce the shrinkage, the nonplastic ingredient may comprise as much as 60 per cent of the total mortar. Sufficient raw clay must be used, however, to give proper plasticity and workability, and therefore the clays must be carefully selected for this purpose. The size distribution of the nonplastic grog also affects the working properties of the mortar. The ASTM Specification C 105-47 covers ground fireclay mortars specifying four classes, depending on the refractoriness of the clay. Heat-setting mortars are usually shipped in 100-lb moistureproof bags.

Air-setting Mortars. Air-setting mortars are composed of a base of precalcined fireclay or raw flint clay crushed to pass a 35-mesh screen. To this is added a plastic fireclay and from 5 to 20 per cent sodium silicate solution. The choice of plastic bond clay and the soda-silicate ratio of the sodium silicate solution will determine the properties of the mortar. To obtain a mortar for severe temperature conditions, a highly refractory clay and a sodium silicate solution that has a low ratio of soda to silica should be chosen. For more moderate temperature service, a more plastic but less refractory clay combined with a sodium silicate solution richer in soda will give a mortar of better working properties and lower vitrifying point, but it will, of course, have a lower temperature use limit. The grog base should be sized so as to produce in the finished mortar the least drying and firing shrinkage compatible with good workability.

The water content of an air-setting mortar is adjusted until it has the consistency of a thick batter. On air drying, these mortars set to a good strength and form an almost monolithic structure with the brickwork, in some cases the mortar joint being stronger than the surrounding brick.

A batch mixing process is generally used to ensure good control of the tempering water added. After mixing, the mortar is packed in steel drums and sealed with rubber-gasketed steel lids. These containers are sold in 50-, 100-, and 200-lb sizes. ASTM Specification C 178-47 specifies three classes of mortar. The mortar must be fine enough to pass 95 per cent through a 35-mesh screen and when used in a joint should give a dry strength of over 200 psi modulus of rupture as measured by ASTM Specification C 198-47.

Recently air-setting mortars have been developed with aluminum phosphate as the bonding agent. Typical of this product is the composition described in the patent by Greger and Reimer.[33] Barium aluminates

as cements have been suggested as having both high setting strengths and refractoriness.

For some special applications, a dry, air-setting mortar is desired. In this case, dry, powdered sodium silicate is used instead of the wet solution, the rest of the mortar remaining essentially the same. The air-set strength of these dry mortars, however, is not so great as that obtained with the wet mortars. Dry, air-setting mortar is packaged in moistureproof bags, usually in 100-lb sizes.

Some manufacturers have had trouble with air-setting mortars hardening in storage, and considerable research has been carried out to find the cause. It is generally believed now that the hardening is due to a base-exchange reaction between the sodium silicate and the natural clay with adsorbed calcium ions.[17] This is brought out in Table 56, derived from some experiments made in the Ceramic Laboratory of the Massachusetts Institute of Technology. It has also been found that clays containing organic matter may develop an acid reaction in storage and thus cause setting.

TABLE 56. HARDENING PROPERTIES OF AIR-SETTING CEMENTS

Adsorbed Ions on Clay	Hardening
Na^+	None
K^+	None
Ba^{++}	None
Ca^{++}	Severe
H^+	Severe

Special Mortars. For special applications, both heat-setting and air-setting mortars are made up using bases other than fireclay. Magnesite, chrome, silica, alumina, and silicon carbide are the more common ones and are used in laying up bricks of their respective materials. Alumina mortars are used where extreme temperature conditions are encountered and where freedom from iron is important. So-called "natural mortars" are much used in Europe. They consist of a naturally occurring clay and sand mixture with good working properties.

Application. Mortar is generally applied in one of three ways, but it should be emphasized that in most cases, the thinnest possible joint is desired. The first method results in the so-called "buttered joint," where the mortar is mixed to a batter consistency and the top of the exposed course of brickwork is spread, using a trowel, with a thin coating. The brick to be laid is given a trowel coating on the bottom of one end and then tapped or pushed into place.

The second is known as the "dip" method. The mortar is thinned out with more water than when using buttered joints. The brick to be laid is dipped into the thin batter on the bottom and one end and then pushed

into place. The thickness of the joint can be regulated by the consistency of the batter. A combination method sometimes used consists of pouring a batter on to the exposed top course and then dipping the bricks to be laid on them. This results in more completely filled joints than the straight dipping method.

Approximately 400 lb of mortar is required for setting 1,000 bricks.

Tests for Refractory Mortars. A number of methods have been proposed for testing mortars,[14] but it is still difficult to get a quantitative measure of the illusive property called workability.

The fusion point can be determined by the methods described in Chap. XIV; but when silicate of soda is present, a preliminary calcining of the material to 1100°C is recommended by Phelps in order to obtain consistent results. However, the fusion point is not particularly valuable, and the block tests as used for glazes and enamels[14] or the amount of flow of the mortar when used as a bond is more important.

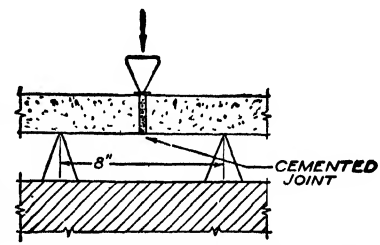


FIG. 164. Method of measuring bonding strength.

The bonding range is generally determined by cementing two half bricks together on the 2½- by 4½-in. faces with a definite thickness of joint. (ASTM Specification C 198-47.) After drying, they are broken as shown in Fig. 164, or they may be heated to various temperatures and broken while heated or when cooled to room temperature. Care must be exercised to prevent any stresses in the samples due to movement of the pieces while drying; otherwise low values will result from fine cracks.

The shrinkage can be measured on bars of the mortar in the usual way or by the characteristics of a layer dried and fired on a brick. The coefficient of thermal expansion can be measured by the methods described in Chap. XVII.

The workability is an important property, but one difficult to measure. Troweling ability is measured by a machine developed by the National Bureau of Standards,[14] but it is generally better to depend on the reports of experienced bricklayers. Rate of settling is important in mortars used in the pouring consistency and is simple to evaluate. Water-retention values, as measured by Phelps, are determined by cementing two half bricks together with no load and then, after a certain time interval, adding a load and noting the amount of mortar squeezed out. This test is particularly important for insulating refractories.

Resistance to erosion by slags or penetration by gases can be measured by methods described in Chaps. XVI and XX, respectively.

3. Plastics. Plastic refractories are now being used in somewhat larger quantities than in the past; in some instances, quite large furnaces have been constructed of monolithic plastic material with good results. It should be noted that the plastic material fires hard only on the hot surface and has a weaker and more flexible zone on the cooler side. Although this may sometimes be a disadvantage, in other cases it actually seems to give a greater life than the burned refractory because of the flexibility of the wall. However, success can be obtained with plastics in large monolithic structures only by skilled application.

Fireclay Plastics. Some of the plastic materials are cold setting; *i.e.*, they develop strength on drying. As in the case of cold-setting mortars, this strength is achieved by the addition of sodium silicate to the mass. Most of the plastics are made up with a base of fireclay grog, either specially prepared or made from waste brickbats and saggers. The maximum size of this grog runs from 4 to 2 mesh in order to reduce the drying and firing shrinkage. The bond clay used must be selected with great care to give good workability and low shrinkage.

It is particularly important that the plastics have a low drying and firing shrinkage; otherwise the structure will be badly cracked after the first firing. For this reason, the proportion of grog is comparatively large, running between 40 and 60 per cent of the total. Not only the maximum size of the grog is important in achieving good results, but the grading of the grog to give the best characteristics is quite important. The plastic mass should be of such consistency that it is coherent and sticks to the brickwork. It should not be crumbly when worked up or get soft and wet when hard rammed. A good plastic can be rammed into a patch in the crown without slumping or pulling away. ASTM Specification C 176-47 calls for two types of plastic varying in refractoriness.

Ladle Mixes. A considerable amount of plastic refractory called "ladle" or "ramming" mixes are used for lining ladles in the iron and steel industry and for pouring spouts and parts of that nature. These refractories must have rather special properties, such as good workability and a softening point approaching the pouring temperature of the metal, so that the surface of the refractory becomes glazed and offers a good resistance to metal and slag attack. Whereas many of these mixes have bases of fireclay grog, others consist of a kaolin base; and in some cases, high-alumina clays have been used.

Special Plastics. Besides the fireclay-base plastics, considerable quantities of chrome-base plastics are used, particularly under conditions of severe slag erosion. The important field for this class of plastics is in the stud walls of boiler furnaces, where it can be rammed around the waterwall tubes to form a refractory capable of withstanding terrific punishment in the way of high temperatures and slag conditions. This type of plastic is

usually made up of raw or calcined chrome ore with some clay bond and often silicate of soda. African or Cuban chrome ore is generally preferred for this use.

Silica ramming mixtures are made from crushed ganister or sandstone and fireclay as a bond. These mixes should be made up to have good workability and are used largely for patching cupolas and other metallurgical furnaces. Silicon carbide ramming mixtures are used where high heat transfer or good slag resistance is desired. Though comparatively expensive, they give excellent service under certain severe conditions. Magnesite ramming mixtures usually consist of dead-burned magnesite grain mixed with some organic bond like tar or dextrine. These are used for the basic electric furnaces, basic open-hearth furnaces, and some of the nonferrous constructions.

Application of Plastics. Satisfactory service cannot be expected from plastic materials unless they are properly applied. The directions given by the maker of the plastic used should be carefully followed in order to ensure a first-class job. Although the methods vary somewhat depending on the type of plastic, in general the following steps should be taken in the application of this material.

In laying a plastic furnace bottom, such as plastic chrome ore in a forging furnace, it is customary to use the following procedure: Take the material out of the cans and dump it on a clean spot on the floor near the furnace, cutting the lumps with a spade but adding no water. If the material has to be left for any length of time, it should be covered with damp burlap bags to prevent its drying out. Beginning on one side of the furnace floor, lumps of the material should be spread out in a layer approximately 50 per cent thicker than the finished layer; *i.e.*, if a 3-in. floor is going to be put in, the thickness of the lump material should be 4 or 5 in. It is well to work in a strip about 30 in. wide beginning at one side of the furnace. A heavy spade then thoroughly cuts through the lumps with deep strokes so that the blanket of material is thoroughly tied together. Then with a heavy tamper, the whole mass is consolidated with heavy strokes. The thickness of the layer should be tested with a rod. If it is too thin, the whole mass will have to be cut up again with a spade before adding more material; otherwise it will not consolidate. The final surface can be put on by laying boards on top and tamping on these. The next 30-in. strip can then be started, care being taken to ensure that it is well cut into the edge of the finished strip to make a bond. More boards can be laid on this, and the procedure repeated until the whole floor is done. The finished surface should not be walked on unless boards are put down.

It is good practice in all plastic construction to punch the layer with small vent holes about 2 in. deep to let out the steam on drying. This can be very conveniently done by making a rectangular frame into which spikes

have been driven on about 3-in. centers. The frame can be readily pressed down on to the surface of the plastic.

In some cases, successful results have been obtained by tamping the hearth while it is hot with a heavy weight on the end of a pipe that can be introduced through the furnace door. If this tamping is carried out every week end, the hearth soon becomes consolidated into an excellent structure.

When using plastic materials in side walls, wooden forms are required in order that the plastic can be rammed in to form a really monolithic

FIG. 165. An example of furnace repairs with a plastic refractory. (*Courtesy of A. P. Green Fire Brick Co.*)

structure. Sometimes plastic materials have been used for small furnace roofs where the ramming is done on top of a form. Generally, however, a refractory concrete would be used for this purpose.

Plastics are also used for patching walls; and under these conditions, great care must be taken to obtain a satisfactory piece of work. The wall itself must be carefully cleaned of any adhering slag, and the brickwork surface roughed up and, in some cases, undercut to hold the patch. This is usually hammered in with a heavy wooden mallet, precautions being used to build up the layer uniformly and without laminations. Fig. 165 shows a patch of this kind which has been completed in a furnace.

Packing of Plastics. Plastics are usually shipped wet in tightly sealed cans, although manufacturers sometimes pack a cube of the mixture in waterproof paper and ship it in a carton. Occasionally, manufacturers

have had trouble with air-setting plastics hardening in storage, as discussed for air-setting mortars.

Testing of Plastics. The important characteristics of plastic materials are the fusion point, the workability, the reheat shrinkage as determined by the panel test, and the strength when fired to various temperatures. The workability is measured as specified in ASTM C 181-47, which seems to give satisfactory results. The work of Heindl and Pendergast[35] may also be referred to.

4. Concretes. Refractory concretes are generally made up with a heavy grog to provide a dense, strong mass or with a porous grog to provide a light refractory. They are widely used for low- and medium-temperature work. Some important applications are the casting of baffles in boiler-tube banks, forming the lining of doors and the tops of tunnel-kiln cars, and, in some cases, the construction of special shapes.

Dense Mixes. These mixes are generally made up with 60 to 80 per cent fireclay grog, perhaps made from crushed brickbats, and 15 to 25 per cent early strength or high-alumina cement and clay for workability. The prepared mixes, of course, are always shipped dry, but often they are made up and mixed by the user, as he generally has available his own brickbats, which can be readily crushed up for grog. It will be found, however, in general, that a carefully prepared batch made by a reliable manufacturer will give better results than mixes made up by the user. Refractory concretes can seldom be used above 2650°F (about 1460°C). ASTM Specification C 213-47 calls for two types, one for high-temperature zones and one for low.

The pure, high-alumina cement described by Pole and Moore,[49] consisting of $3CaO{\cdot}5Al_2O_3$, would seem to have some advantage in raising the use limit of refractory concretes.

Lightweight Mixes. These mixes are made up in a similar way to the previous ones, except that the aggregate is of some lightweight material like lumps of infusorial earth, bloated clay, or porous grog. Lightweight mixes are used in such places as doors of furnaces and similar positions where the temperature is not extreme. Their density runs between 45 and 60 lb per cu ft.

All the refractory concretes have a low strength at a temperature of 1500 to 1800°F (about 820 to 980°C), where the cement is dehydrated and strength has not been attained by vitrification. This will give a weak layer in the structure that has not yet been overcome in this class of material. Nevertheless, these mixes are being used with considerable success in many types of structure.

Tests. The tests of refractory concretes are similar to those mentioned for plastics, *i.e.*, the softening point, the drying and firing shrinkage, and the strength at various temperatures.

5. Coatings. Refractory coatings are used to some extent on the surface of certain types of brickwork to close the pores and present a more homogeneous surface, thus minimizing abrasion and slag erosion. However, unwarranted claims have been made for coatings, claims indicating that a good coating would make a lower grade refractory give the service of a high-grade refractory. This is not generally true, and a coating is by no means a cure-all for refractory troubles.

Natural Coatings. Raw fireclay, which was used to some extent in the early days, has been more or less discarded because of its high shrinkage and tendency to peel off the brickwork. Natural coatings are used extensively in Europe containing clay, quartz, and feldspar in such proportions as to reduce the shrinkage and give a fluxing action. This material is very similar to the natural mortars previously discussed and generally has good working properties with a comparatively low cost.

Prepared Fireclay Coatings. For high-temperature conditions, the coating used most frequently is a mixture of calcined grog with a plastic bond clay. A satisfactory coating should have a low shrinkage and adhere well to the brick so that no peeling or checking is observable on heating to the working temperature. The brick manufacturers' recommendation should be taken, because a coating that may work very well with one type of refractory may not work at all with another type, even though of very similar properties.

Special Coatings. Many special coatings are available such as those with a chromite base or a chrome oxide base which are used to give some additional slag resistance to fireclay or insulating firebrick. There are also coatings having fused alumina or silicon carbide as a base for special purposes. They all must have the property, however, of low shrinkage and adherence to the brick with which they are used.

Application of the Coatings. Coatings can be applied to the brickwork with a brush or with a spray gun. The latter is generally more satisfactory in giving a really good job. The coatings must be applied in comparatively thin layers, $\frac{1}{16}$ to $\frac{1}{8}$ in. being the maximum generally used. Even then, a better job is obtained by applying it in several successive applications if this is possible. About $\frac{1}{4}$ to $\frac{1}{2}$ lb per sq ft of material should be allowed for an average coating job. Particular care should be taken that the brickwork is clean and free from dust before the coating is applied.

CHAPTER XII

SOME SPECIAL REFRACTORY MATERIALS

1. Introduction. Since the previous edition of this book was published, considerable material has become available on special, high-temperature refractory materials, which, though as yet too costly for tonnage use, have great interest for small-scale applications. These include the pure oxides, carbides, nitrides, borides, and sulfides of high stability. In particular, developments have been rapid in the production of low-porosity bodies from them with little or no fluxes. These bodies are so valuable for certain purposes that a new chapter dealing with them has seemed justified.

2. Refractory Metals. The refractory metals may be divided into two classes: the noble metals that can be heated in air and the tungsten metals for use in a vacuum, neutral, or reducing atmosphere. The former include ruthenium, rhodium, palladium, osmium, iridium, and platinum. Of these, only platinum is plentiful enough for any large-scale use, and it is unfortunate that it does not have a higher melting point. In addition to its laboratory use, it is finding an increasing place in the glass industry for fiber glass and optical glass manufacture. Pots holding up to 100 lb of glass are lined with this metal, and it is said that a small continuous tank is in operation with a complete platinum lining.[155] Because there is no solution of the container, optical glass of very fine quality is claimed. Platinum also has the advantage of being ductile, so that it can be readily formed into any shape.

The second class of metals include tungsten, rhenium, tantalum, molybdenum, columbium, thorium, titanium, vanadium, zirconium, and hafnium. The true melting point of many metals is still not well known. For example, the value for tantalum has gone up from 2850[3] to 2996°C[4] in the last few years, and that for uranium has gone down from 2100[165] to 1150°C.[179] The most useful of these metals are tungsten, tantalum, and molybdenum. The first is most refractory but is difficult to fabricate. Molybdenum can be formed and welded in simple shapes, while tantalum is quite ductile and can be formed into complicated structures. Any of them can be formed by powder metallurgy methods in much the same way as the oxides.

The low vapor pressures of tungsten and tantalum (as shown in Fig. 166) make them particularly suitable for high-temperature work in a vac-

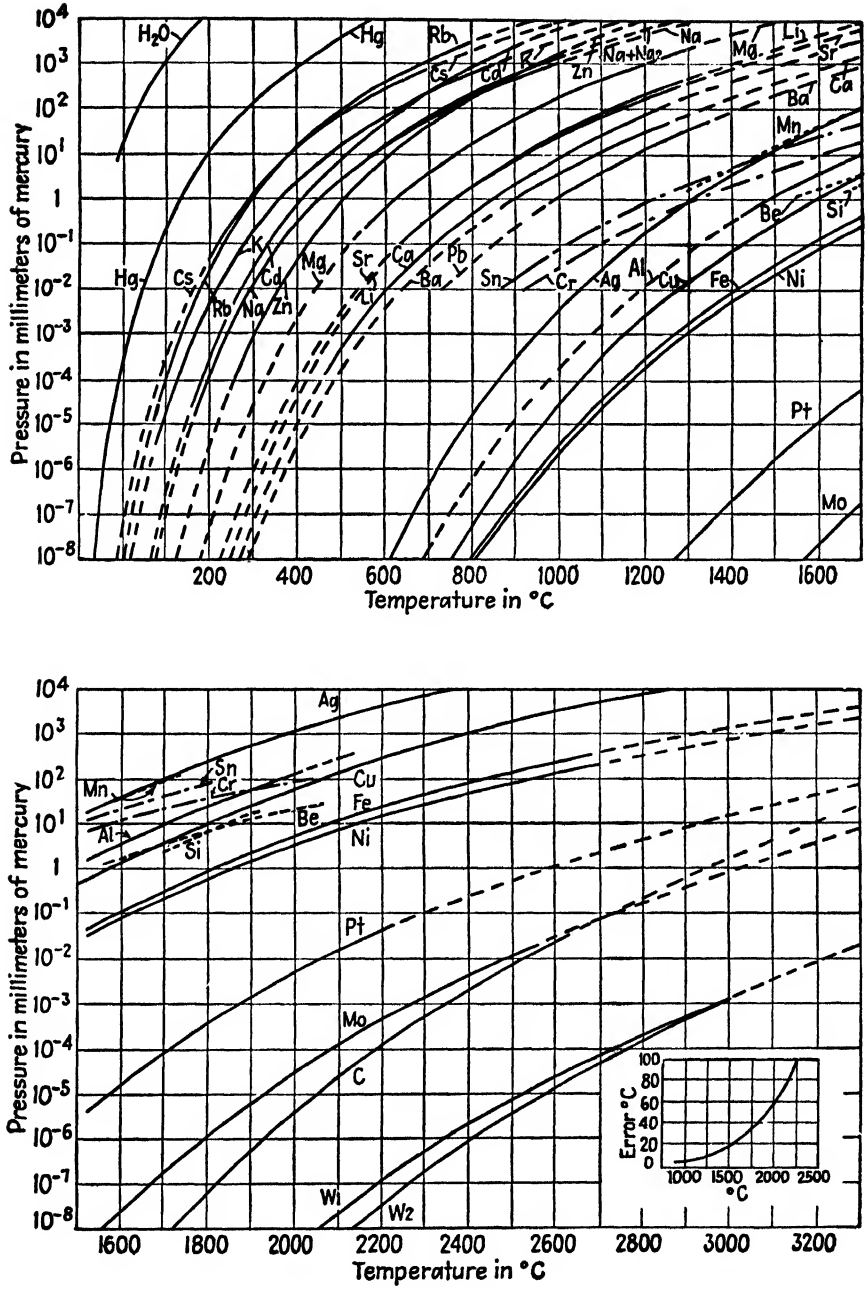


FIG. 166. Vapor pressures of elements at elevated temperatures.

uum. In Table 57 are shown the important properties of the refractory metals.

3. Refractory Oxides. The oxides are particularly valuable, as they are stable in air as well as in less active atmospheres.

Alumina. This oxide is one of the easiest of all to vitrify by means of the solid reaction, and much ware has been made both here and abroad in the form of a pure, nonporous, translucent body with excellent mechanical, electrical, chemical, and refractory properties.

The manufacture seems to follow the original German development of "Sinterkorund," a description of which is given in Report P.B. 18776.[11]

The raw material is a chemically pure calcined alumina (α-alumina) containing about 0.1 per cent Fe_2O_3, 0.1 per cent MgO, and 0.2 per cent CaO. This is ground wet in a steel ball mill for 50 to 75 hr until the maximum particle size is 12 to 15 μ and 65 per cent is below 5 μ. The suspension is then digested with 10 to 15 per cent of hot HCl (200 liters of acid to 100 kg of Al_2O_3) for one or more days, then water washed three or four times to eliminate the soluble iron and leaving the suspensions slightly acid. We have found in our laboratories that if the freshly ground slip is passed through a magnetic separator, the acid treatment is greatly shortened. To flocculate the suspension so that it will settle after washing may require the addition of a base to raise the pH. If the grinding is carried out in alumina mills the acid washing is eliminated.

The forming may be done by slip casting into plaster molds. The German practice uses a slip with a specific gravity of 2.0, but we have found it possible to make casts with slips having a specific gravity as high as 3.0 and with a pH of 4.5. P. D. Johnson has shown that alumina gel can be precipitated on the alumina particles, after which casting slips can be made with a pH of 9, much like clay slips. Forming can also be carried out by dry pressing in steel molds with organic binders or lubricants such as wheat flour, gum tragacanth, polyvinyl alcohol, waxes, or rubber latex. Extrusion is also possible if the binder content is high enough. By mixing the alumina with a heated synthetic resin (thermoplastic), injection molding into a cooled die is possible to give an accurately sized piece with a polished surface. The previously mentioned report[11] gives the formula used by Bosch for this purpose as taken from the Bosch patent B489,981 (German). By using the proper binders, the dried ware can be accurately turned to size as is common practice with electrical insulators.

The firing in Germany takes place in pure, fused magnesia muffles heated by surface combustion, using city gas and preheated air to temperatures of 1900 to 1950°C and held for 1 to 3 hr. It seems to be common practice to use 0.5 per cent MgF_2 to prevent the growth of large crystals, but most of the fluorine should be eliminated in the firing. If porous ware

TABLE 57. PROPERTIES OF REFRACTORY METALS

Material	Formula	Sp gr, g per cc	Hardness*	Tensile strength, M psi	Young's modulus of elasticity, Million psi	Mp, °C	Solubility[179]†
Actinium.....	Ac (227)					1800 d.[179]	
Boron.....	B (10.82)	2.3[176]	9.5 M[167]			2300 ± 300[176]	i. H_2O;s. HNO_3, H_2SO_4;i. al.,eth.,alk.
Carbon..... (graphite)	C (12.01)	2.22[176]			0.7[176]	3700 ± 100[176]	i. H_2O;s. liq. Fe; i. a.,alk.
Columbium.....	Cb (92.91)	8.57[176]	75 Br[4] 10 Sc			2000 ± 50[176]	i. H_2O;s. h. H_2SO_4;sl. s. HF; i. HCl,HNO_3
Hafnium.....	Hf (178.6)	11.4[176]				1700[168]	i. H_2O
Iridium.....	Ir (193.1)	22.4[168]	6.5 M[167]		74 7[170]	2454 ± 3[172]	i. H_2O; amor. s. aq. reg; i. a.,aq. reg.
Masurium.....	Ma (98–99.5)	11.5				2300[179]	
Molybdenum....	Mo (95.95)	10.2[168]	147 Br[4] 12 Sc	260 to [4] 350	50[176]	2625 ± 50[176]	i. H_2O;s. h.conc. HNO_3,H_2SO_4;i. HCl,HF,dil. H_2SO_4,NH_3
Osmium.....	Os (190.2)	22.48[168]	7 M[167]			2700 ± 200[172]	i. H_2O;sl. s. HNO_3,aq. reg.; i. NH_3
Platinum.....	Pt (195.23)	21.45[168]	35–90 Br[4] 18 Sc 4.3 M[167]	35 to [4] 53	22[176]	1773.5 ± 1[176]	i. H_2O;s. aq. reg.,fus. alk.
Rhenium.....	Re (186.31)	20[176]				3000[168]	s. conc. HNO_3,H_2O_2
Rhodium.....	Rh (102.91)	12.44[176]			42.5[57]	1966 ± 3[176]	i. H_2O;s. H_2SO_4 + HCl.h. conc. H_2SO_4;sl. s. a..aq reg
Ruthenium.....	Ru (101.67)	12.2[168]	6.5 M[167]			2500 ± 100[176]	i. H_2O;sl. s. a.,aq. reg.;i. al.,eth.
Tantalum.....	Ta (180.88)	16.6[168]	75 Br[4] 10 Sc	130 to [4] 178	27[176]	3000 ± 100[176]	i. H_2O;s. HF,fus. alk.;i a.
Thorium.....	Th (232.12)	11.5[176]				1800 ± 50[176]	i. H_2O;s. HCl,H_2SO_4,a2. reg.,sl. s. HNO_3
Titanium.....	Ti (47.90)	4.54[176]	18R B to [6] 25 Rc	80 to [6] 120	12.1[176]	1820 ± 100[176]	i. H_2O;s. d. a.
Tungsten.....	W (183.92)	19.3[176]	290 Br[4] 40 Sc	490 to [4] 600	50[176]	3410 ± 20[176]	i. H_2O;s. h. conc. KOH;sl. s. HNO_3,aq. reg.
Vanadium.....	V (50.95)	5.68[176]				1735 ± 50[176]	i. H_2O;s. HNO_3,H_2SO_4,HF,aq. reg.;i. HCl,alk.
Ytterbium.....	Yb (173.04)					1800[176]	d. H_2O(ev. H_2)
Zirconium.....	Zr (91.22)	6.4[168]	85 Br[6]	42 to [6]	10.7[6]	1860 ?[6]	i. H_2O;s. HF,aq. reg.;sl. s. a.

* M. Moh's scale. Rc. Rockwell C. Rb. Rockwell B. Br. Brinell.
† See list of abbreviations Table 63, pp. 318–321.

TABLE 57. PROPERTIES OF REFRACTORY METALS (*Continued*)

Material	Bp, °C	Vapor pressure, mm Hg	Sp heat, cal per g	Lin. coef. of therm exp, °C × 10^6	Coef. of therm. conduct., cal per sec per sq cm per °C per cm	Resistivity, ohms per cc × 10^{-6}	Solubility[174]†
Actinium	1700 d.[170]						
Boron	2550[175]		0.309[176]	2[168]		1.8×10^{12}[168]	i. H_2O;s. HNO_3, H_2SO_4;i. al.,eth.,alk.
Carbon	4827[175]	10^{-7} (1800°C)[169]	0.165[176]	0.6–4.3[176]	0.057[170]	1400[168]	i. H_2O;s. hq. Fe;i. a.,alk.
(graphite)	sub.	10^{-2} (2500°C) 1 (3000°C)					
Columbium	3300[175]			7.1[176]		20[170]	i. H_2O;s. h. H_2SO_4;sl. s. HF;i. HCl,HNO_3
Hafnium	5395[175]						i. H_2O
Iridium	4900[175]		0.032[176]	6.5[168]	0.141[170]	5.3[168]	i. H_2O; amor. s. aq. reg;i. a.,aq. reg.
Masurium							
Molybdenum	3560[173]	10^{-6} (1500°C)[169] 10^{-4} (2000°C) 10^{-2} (2500°C)	0.065[176]	4.9[176]	0.350[170]	5.17[176]	i. H_2O;s. h.conc. HNO_3,H_2SO_4;i. HCl,HF,dil. H_2SO_4,NH_3
Osmium	5604[175]		0.031[167]	6.1[168]		9[176]	i. H_2O;sl. s. HNO_3,aq. reg.;i. NH_3
Platinum	3910[167]	10^{-6} (1500°C)[169] 10^{-4} (1700°C)	0.032[176]	8.9[176]	0.166[170]	10 (20°C)[167] 26 (400°C)	i. H_2O;s. aq. reg.,fus. alk.
Rhenium	5871[175]		0.035[176]	12.5[176] 4.7		21[170]	s. conc. HNO_3,H_2O_2
Rhodium	4500[175]		0.060[175]	8.1[176]	0.213[170]	4.69 (0°C)[167] 6.6 (100°C)	i. H_2O; s. H_2SO_4 + HCl,h. conc. H_2SO_4;sl. s. a.,aq. reg.
Ruthenium	4900[175]		0.061[176]	9.1[176]		10[168]	i. H_2O;sl. s. a.,aq. reg.;i. al.,eth.
Tantalum	6100[175]		0.036[176]	6.6[176]	0.130[170]	14.6[176]	i. H_2O;s. HF,fus. alk.;i. a.
Thorium	5200[175]		0.028[176]	11.1[176]		18.6[176]	i. H_2O;s. HCl,H_2SO_4,a.; reg.,sl. s. HNO_3
Titanium	5100[175]		0.142[176]	8.5[176]		3[168]	i. H_2O;s. d. a.
Tungsten	5390[175]	10^{-8} (2000°C) 10^{-6} (2500°C) 10^{-3} (3000°C)	0.034[170]	4.3[176]	0.476[170]	5.51 (20°C) 98.9 (2700°C) 118 (3200°C)	i. H_2O;s. h. conc. KOH;sl. s. HNO_3,aq. reg.
Vanadium	3000[175]		0.115[176]			26[170]	i. H_2O;s. HNO_3,H_2SO_4,HF,aq. reg.;i. HCl,alk.
Ytterbium							d. H_2O(ev. H_2)
Zirconium	5050[175]		0.066[176]	5.6[176]		41[176]	i. H_2O;s. HF,aq. reg.;sl. s. a.

† See list of abbreviations Table 63, pp. 318–321.

is permissible, then lower firing temperatures can be used. Firing in a neutral or oxidized atmosphere seems necessary as shown in the Siemens and Halske patent B339,726 (German).

The properties of sintered alumina ware are given at the end of this section, indicating its low porosity and high strength. These properties have made it particularly valuable as pyrometer tubes, spark-plug insulators, and crucibles for melting metals or glasses.

TABLE 58. PURITY OF COMMERCIAL BERYLLIUM OXIDE

Constituent	Light fluffy*	High-fire standard purity*	Refractory grade†	$Be(OH)_2$†
BeO‡	99.8	99.8	99.3	53.5
SiO_2		0.09	0.22	0.01
Al_2O_3	0.01	0.01	0.22	0.01
Fe_2O_3	0.10	0.10	0.07	0.01
MgO	0.02	0.02	0.12	0.01
CaO	0.02	0.02	0.02	0.01
MnO			0.005	
Alkalies	0.02			0.01
Ignition loss				46.5

* Brush Beryllium Company.
† Clifton Products Company.
‡ By difference.

Beryllia. Considerable research has been done on pure, dense beryllia ware in the Ceramic Laboratory at the Massachusetts Institute of Technology. The details will be quoted at some length[22] from the *Journal of the American Ceramic Society.*

TABLE 59. PROPERTIES OF BERYLLIUM OXIDE

Melting point	2510°C
Specific gravity	3.0
Hardness	9
Thermal conductivity	Very high
Heat-shock resistance	Excellent
Thermal expansion (mean up to 1400°C)	9.3×10^{-6}°C
Vapor pressure (at 2080°C)	1.8×10^{-3} mm Hq.

Raw Materials. The production of BeO from beryl is completely described by Potvin[20] as carried out in the Degussa plants in Germany, and the ore resources and output are discussed in P.B. 60,386.[16] The purity of available BeO materials is shown in Table 58, and the properties of pure BeO are given in Table 59. Most of this research was carried out with the highly purified hydroxide described in the last column.

The melting point of the highly purified oxide may be somewhat higher than the figures given in the literature. When the oxide is heated in a combustion furnace, it is volatile at temperatures as low as 1800°C; small crucibles fired several hours at this temperature may lose 50 per cent of their weight. The hardness of the fused material is about the same as or greater than that of sapphire, and instances have been noted where it even

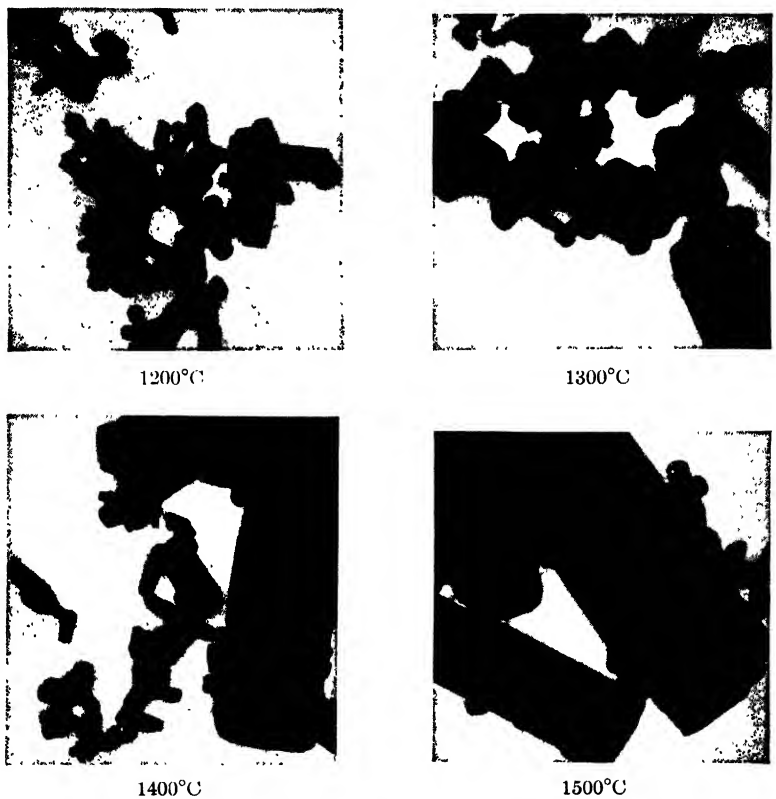


FIG. 167. Electron microscope photomicrographs of beryllia crystals as affected by calcining temperature. (*Note:* These photomicrographs are similar, but not identical with those in the original article.)

scratched a boron carbide mortar. The thermal conductivity has been reported to be relatively very high compared with other oxides. More work must be done to obtain quantitative data on the thermal conductivity of BeO, but it is known that its heat-shock resistance is unusually good.

Calcining $Be(OH)_2$. Early work on pressing bodies was carried out with the oxide, but a variability from batch to batch made consistent production impossible. The next step was to calcine the hydroxide at various tem-

peratures to find the conditions best suited to molding dense crucibles because the inherent crystal size is known to increase with calcining temperature.

Electron microscope photographs in Fig. 167 show the beryllia crystals clearly. At 1200°C calcination temperature, most of the crystals are 0.05 to 0.2 μ in size. At 1300°C, many crystals are of the same size, but a number of them are 1.0 to 2.0 μ long. At 1400°C, a few small particles still exist but large ones predominate 2.0 to 4.0 μ long; and at 1500°C, the mass

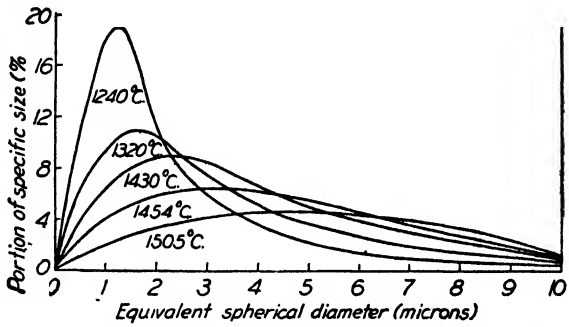


FIG. 168. Particle-size distribution of beryllia calcines determined by sedimentation methods.

consists entirely of crystals 2.0 to 4.0 μ long. The particle-size distribution by sedimentation, as shown in Fig. 168, gives somewhat different results, because clusters are measured rather than individual crystals. The increasing size with temperature, however, is clearly indicated.

The mechanism of crystal growth is a solid reaction whereby atoms or atom groups are dislodged from the crystal face by thermal agitation. Those atoms then are attracted to another nearby face and fall into a position to give the minimum surface energy. As large faces attract atoms more strongly than small ones, the large crystals grow at the expense of the small ones. Owing to the high vapor pressure of BeO in combustion gases, the growth is quite rapid.

Forming Procedures. A refractory body was readily made by bonding high-temperature calcine or fused grog with about one-third of its weight of fine, low-temperature calcined oxide. The mixture was blended with water without a binder and tamped in a mold. For more complicated shapes, an organic binder was required, and David[18] suggests the use of a 4 per cent solution of $BeCl_2$ for this process.

Drain castings were made in plaster molds by the same casting technique used for clay slips. The 200-mesh fused oxide was ball milled in a 3.5-gal steel mill, the charge being 21 kg of nickel-steel balls, 4 kg of beryllia, and 2.4 kg of water. The mill was rotated at 60 rpm for 25 hr to produce

the particle-size distribution shown in Fig. 169. In the grinding process, a considerable amount of iron was picked up, which was leached out with hydrochloric acid. Three acid treatments and washings were used, and the slip was left with a pH between 4.5 and 5; this should be checked before casting. The specific gravity of the casting slip was 1.9 to 2.0, representing 37 to 33 per cent water, respectively.

Pressed ware has the advantage that it can be made nonporous, an important feature in melting crucibles.

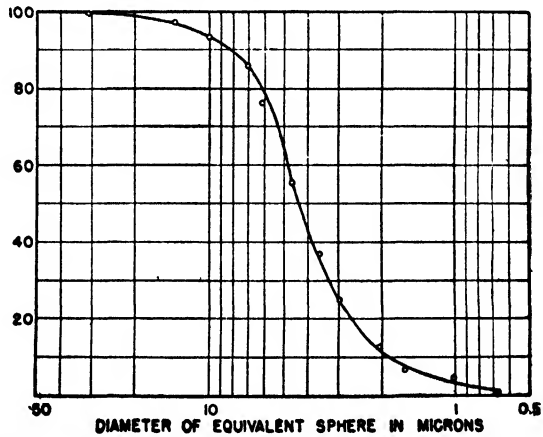


FIG. 169. Typical particle-size distribution for beryllia casting slip.

To press a hard abrasive powder such as beryllia requires an efficient lubricant. Many are available, but satisfactory results were obtained by the use of a water-soluble wax, such as Carbowax 4000, a polyethylene glycol with a molecular weight of 4000. Fourteen per cent of the dry wax was added to the dry ball-milled powder as a 20 per cent solution in water and was thoroughly incorporated. The mix was then partially dried at 80°C, nodulated by rubbing through a 14-mesh screen, and then completely dried, ready for pressing. Antisticking agents were found necessary in order to remove the piece from the die. Daxad No. 23 in the amount of 0.1 per cent of the mix was satisfactory.

Pressing was done in a carbon-chrome steel mold, heat-treated at 58 to 62 Rockwell C hardness. A typical die is shown in Fig. 170. The working surfaces were lapped to a high polish, and a slight taper permitted easy removal of the finished piece. The molding was done in a hydraulic press at 20,000 to 30,000 psi, and a weighed amount of mix was used to produce uniform size of piece.

The pressed pieces were strong and had a highly polished surface. In this state, they could be machined to close tolerances with tungsten carbide tools.

Firing Procedure. To remove the wax from pressed ware, the piece was placed in a closed sagger of insulating firebrick and heated uniformly for a period of 8 hr until a maximum temperature of 500°C was reached. The removal of the wax is a critical operation and must be carefully controlled or cracking will result. The wax may be removed at a much lower temperature in a vacuum.

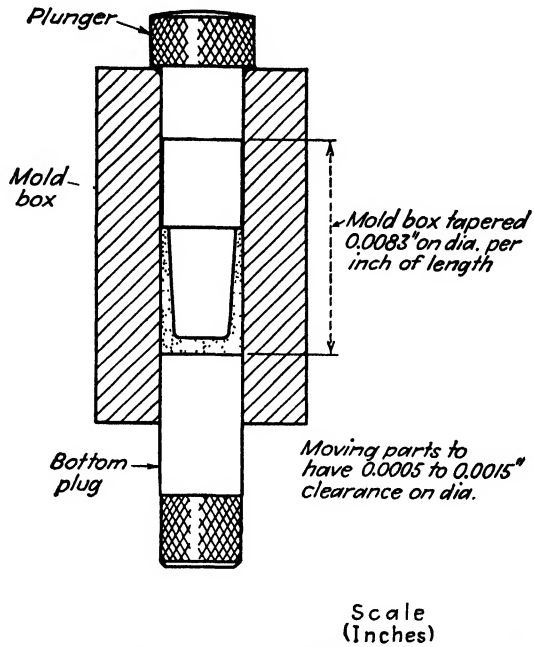


FIG. 170. Steel die used in preparing beryllia crucibles.

Cast pieces can be prefired to 1000°C to make them strong enough for finishing.

The preheated ware was next fired to 1800°C and held at this temperature for 30 min to give a maximum density. The rate of heating depends on the size of the piece (small pieces can be fired in 4 or 5 hr). The firing was carried out in catenary kilns made of fused-alumina brick and fired by premixed city gas and cold air to a temperature of 1800°C. A small alumina furnace was also used, which was fired by oxygen and propane where temperatures of 2000°C could be reached. Some runs were made in a vacuum with high-frequency heating. Beryllia is volatile at this temperature, since weight losses of 2 to 4 per cent were usual, while some crucibles, which were fired for several cycles, lost over 50 per cent in weight. The vaporized beryllia condensed in the cooler portions of the furnace.

Little is known definitely about the way in which the pores between the crystals close up, but there seem to be two steps. The first is the approach to a spherical pore either by surface flow due to surface-tension forces or by transfer in the vapor state from the long radius of curvature portions to the more highly curved parts where they may adhere with a lower surface energy. The second step is closing the pore itself by some sort of solid flow under surface-tension forces. It is well known that at very low stresses, pure metals flow viscously, probably by migration of lattice defects. The same may well occur in the heated BeO crystals. The gas in the pores escapes by interconnecting passage until the end, where a small volume is trapped in the remaining closed pores.

If ware with some porosity is required, the firing temperature can be lowered; even 1500°C gives a fairly strong piece.

Properties and Uses. The dense BeO showed no dye absorption but had some closed pores, since the bulk density ranged from 2.7 to 2.9 rather than the theoretical value of 3.0. The body was translucent in thin sections, and the surface was pure white and smooth.

Beryllia is a particularly valuable refractory because of its high working temperature—500°C (about 930°F) above pure alumina—so that it may be used as cores for tungsten-wound furnaces, insulation in high-frequency induction furnaces, and insulators in radio tubes. Its high thermal conductivity gives it excellent heat-shock resistance, and its high stability makes it a valuable crucible material for melting pure metals such as iron, nickel, and the platinum metals. Claussen[15] and Kirby[54] claim that it is suitable for melting pure beryllium. Also it has been suggested for melting glasses and slags.

BeO is more inert in contact with C or CO than is MgO and thus can be used up to 2000°C[17] as supports and shields with graphite heaters in the induction furnace. Beryllia is claimed to have excellent hot strength[11] and therefore should be valuable in the jet-propulsion field. Also this oxide has nuclear properties that make it of great value in atomic power development.

Attention is called here to the extreme health hazard in using beryllium and its compounds. As yet, little is known about the toxic effects, but evidence points to the fact that certain individuals are susceptible to dust or vapors of the metal or its compounds, which causes a serious lung condition. Extreme precautions should therefore be taken to have ample ventilation for any dusty process and to carry off all fumes from furnaces.

Thoria. This oxide, because of its high fusion point, is difficult to fire to a dense mass when of high purity. Except for a higher firing temperature, the procedure described for beryllia can be followed in forming small objects. Swanger and Caldwell[40] describe tamped crucibles of fused

thoria moistened with a 20 per cent solution of $ThCl_4$ to form a dense body with an apparent density of 9.5 to 9.7 when fired at 1800°C. Richardson[42] describes the casting of thoria crucibles in plaster molds with P_2O_5 as a deflocculant and also a furnace for firing them at 1900°C.

The main use of thoria would be for extremely high temperature use in an oxidizing atmosphere or vacuum, such as melting the platinum metals. On the other hand, as it is a fissionable material, its use may have future restrictions. Richardson[42] also states that pure zirconium, thorium, iron, and uranium can be melted in thoria without wetting it. Swanger and Caldwell[40] state that osmium can be melted in thoria.

Thorium compounds should be handled with care, because on being stored in closed containers, they produce radioactive gases that are a possible health hazard. Therefore, a container of such compounds should only be opened under a hood or in the open air.

Magnesia. This plentiful and highly refractory oxide is perhaps the most promising for work in the high-temperature field. However, it must be of high purity and therefore requires very high firing temperatures to vitrify. The rate of crystal growth on heating is given by Birks and Friedman.[25] One to two per cent silica is helpful in bringing down the firing temperature and extending the maturing range.

The casting of MgO is possible in water suspensions but difficult because of the rapid hydration. The method of making slips with absolute alcohol developed at the Bureau of Standards[45] works very satisfactorily. Extrusion with a cellulose acetate bond is described by Partridge and Lait.[44]

The high thermal expansion of magnesia, however, makes it rather sensitive to thermal shock; and at elevated temperatures, it reacts with carbon, forming magnesium vapor and carbon monoxide. In a vacuum, its high vapor pressure causes it to volatilize rather rapidly above 2000°C. Swanger and Caldwell[40] state that magnesia crucibles are suitable for melting Ni, Fe, Cu, and Pt without contamination.

Zirconia. This oxide is relatively plentiful and has a melting point about 500°C above alumina, thus making an excellent high-temperature refractory. Because of the rapid inversion of the pure oxide on heating and cooling, it is very sensitive to temperature changes and for practical use must be stabilized by additions to maintain the cubic lattice. The work of Pole, Bernbach, and Gilbert[31] showed that the inversion could be reduced or eliminated by additions of CaO or MgO. However, Curtis[32] showed that the most heat-shock-resistant body had the inversion only partially eliminated and suggested additions of (1) 8 to 12 per cent CaO, (2) 6.7 per cent CaO, plus 3.7 per cent MgO and (3) 2.3 per cent CaO plus 6.4 per cent MgO. Several companies are now marketing stabilized zirconia, probably with somewhat the above additions.

Few data are available on the production of dense zirconia bodies, but the procedure outlined for beryllia would probably be satisfactory here. In fact, Thompson and Mallet[45] describe a method of casting zirconia crucibles as well as ramming with a $ZrCl_4$ bond.

Titania. There is little data on pure TiO_2 as a refractory, for most of the published work is concerned with it as an ingredient in electrical insulators. However, with a melting point of 1850°C it might have value for special purposes. Siemens describes a dense sintered TiO_2 body prepared like alumina. Reduction of TiO_2 to the suboxide TiO occurs readily in the presence of CO or H_2.

Chrome Oxide. The pure oxide is seldom used as a refractory but can undoubtedly be used where it is not subject to reducing conditions. On the other hand, the high vapor pressure is a disadvantage. Some work is now being carried out in the Ceramics Laboratory of the Massachusetts Institute of Technology on the production of dense ware from this material as crucibles for melting.

Lime, Baria and Strontia. These oxides have high fusion points but are subject to hydration. It is possible, however, to form dense, pure refractories from them in the same way as for magnesia.

The Rarer Oxides. There are a number of rarer oxides of high melting point such as CeO_2, La_2O_3, Y_2O_3, and HfO_2 that would undoubtedly make excellent refractories if they were more available. Perhaps some of them have properties that would make them useful in the laboratory even in small amounts. There is little information concerning them now, but their properties should be determined.

The Spinels. The spinels of high melting point, magnesia spinel ($MgAl_2O_4$), barium spinel ($BaAl_2O_4$), and chrysoberyl ($BeAl_2O_4$), can all be readily prepared by solid reaction of the constituent oxides, in some cases assisted by boric acid as a fugitive flux.[33] It has been claimed that spinels can be formed only by amorphous starting materials, but this is not strictly true.

There is no reason to believe that these compounds cannot be formed into dense bodies in the same way as described for beryllia. In general, they are quite resistant to attack by slags and glasses and should be excellent refractories. However, we need to know more about their properties.

A patent of General Motors, British Patent 509,516, describes a spinel series with Mn, Ni, or Co that can be fired to a dense body for a spark-plug insulator.

The High-temperature Silicates. $ZrSiO_4$, Be_2SiO_4, Mg_2SiO_4, and Ca_2SiO_4 all have high fusion points and for some purposes are excellent refractories. Their forming and firing are similar to the methods described for alumina or beryllia. Some of their properties are given at the end of this section.

The High-temperature Zirconates. $ThZrO_4$, $BaZrO_3$, $CaZrO_3$, $MgZrO_3$, and $SrZrO_3$ are all high-melting-point compounds on which little information is available. The work of Pole, Bernbach, and Gilbert[31] gives some properties of these refractories.

Phosphates. Henry[67] has suggested cerium and zirconium phosphates as refractories, but they seem unstable and gradually lose P_2O_5. A few other phosphates are shown in Table 60, but little is known of their stability.

TABLE 60. SOME REFRACTORY PHOSPHATES[168]

Compound	Molecular weight	Melting point, °C	Specific gravity
$Ca_5P_3ClO_2$	520.88	1530	3.17
$CaF_2 \cdot 3Ca_3P_2O_8$	1,008.84	1630	3.18
$10CaO \cdot 3P_2O_5$	986.844	1540	2.89
$Ca_4P_2O_9$	366.328	1630	3.06
$Ca_3(PO_4)_2$	310.258	1670	3.14
$BaF_2 3Ba_3P_2O_8$	1,981.84	1670	
$BaCl_2 \cdot 3Ba_3P_2O_8$	2,014.76	1584	5.949

4. Refractory Porcelains. A porcelain body is distinguished from a pure oxide body in general by having small amounts of other materials mixed with the principal oxide to lower the maturing temperature, increase the maturing range, or control the crystal growth. In the early development of refractory porcelains, it was recognized that the glassy phase must be minimized or eliminated and the crystal size kept small.

An improvement over the usual feldspathic porcelain was the Marquardt body having a composition of 35.12 per cent SiO_2, 63.20 per cent Al_2O_3, and 1.65 per cent K_2O.[71] Some years later when Bowen and Grieg discovered that the stable crystal in the alumina-silica system was mullite ($Si_2Al_6O_{13}$), porcelains with the composition 28 per cent SiO_2 and 72 per cent Al_2O_3 were found much superior to others for laboratory ware, spark plugs, and thermocouple protection tubes. However, to reach maturity at commercial temperatures a small amount of flux was often used.

While it is generally believed that the pure alumina body previously described gives a structure with the optimum properties, the high firing temperature has caused many experimenters to develop other bodies with lower maturing temperatures, particularly in the field of spark-plug insulators. For example, Jeffery (French Patent 405,270) adds a small amount of lime, magnesia, and silica; Fessler and Schwartzwalder (British Patent 546,770), 10 to 25 per cent silica and 1 to 9 per cent magnesia; McDougal, Schwartzwalder, and Fessler (British Patent 546,759), beryllia and silica; McDougal, Fessler, and Schwartzwalder (British Patent 372,939), 0.5 per

cent Cr_2O_3; Bosch (German Patent 705,679) kaolin and silica; and Fessler and Schwartzwalder (French Patent 368,968), 1 to 15 per cent zircon.

Much work has been done on zircon porcelains—mainly, however, for high electrical properties. Russell and Mohr[76] give some excellent data on these bodies.

Considerable interest has been shown in cordierite bodies containing theoretically 13.78 per cent MgO, 34.84 per cent Al_2O_3 and 51.38 per cent SiO_2, because of their very low coefficient of expansion. Wisely and

TABLE 61. PORCELAINS WITH LESS THAN 0.1 PER CENT ABSORPTION[71]

Composition, moles			Maturing temperature °C range	Linear shrinkage, range	Absorption	Coefficient of expansion, 700-800°C	Relative thermal conductivity	Crushing strength, M psi
MgO	BeO	Al_2O_3						
1	24	1	1600 1725	15.5–17.6	0.1	10.8	9	169
1	16	1			0.1		7	
1	8	1	1625–1725	13.6–14.4	0.1		5	152
1	4	1	1680–1725	11.2–12.0	0.1	9.4	4	142
1	2	1	1650	9.7	0.1			
4	96	1	1500–1635		0.1	10.3	11	105
4	48	1	1500–1635	16.8–19.4	0.1		11	
4	24	1	1600–1630	14.4–20.5	0.1		12.5	133
4	16	1	1630	15.5–20.0	0.1		9	
BeO	Al_2O_3	ThO_2						
160	2	1	1650		0.0	10.4	25	244
48	1	1	1750		0.02			279
BeO	Al_2O_3	ZrO_2						
8	1	2				9.3		

Gobler[77] give some results on this body, finding that B_2O_3 and P_2O_5 are the best mineralizers.

Beryl porcelains also have low expansion coefficients as shown by Hummel and Henry.[72] A composition of 80 per cent natural beryl and 20 per cent Florida clay, when fired to 1300°C for 9 hr, had an expansion of about 1.0×10^{-6} (twice that of fused quartz) but deformed above 1350°C, so it would not be useful for really high temperatures.

The most thorough study in the field of high-temperature porcelains is the work of Geller and his associates at the National Bureau of Standards.[71] Some of the more promising bodies in the field of MgO–BeO–Al_2O_3, together with their properties, are given in Table 61.

The system BeO–Al_2O_3–ThO_2 showed complete vitrification in only a limited range up to 1800°C, but probably higher maturing temperatures would give other excellent porcelain bodies.

In the system Be–Al_2O_5–ZrO_2 there were no vitrified bodies up to 1800°C, but here again it would be expected that excellent bodies might result from higher firing temperatures.

In Table 62 are shown some high-melting eutectic compounds that might be of interest in the development of porcelains. In Table 63 are shown the important properties of the refractory oxides.

TABLE 62. SOME HIGH-MELTING EUTECTICS[71]

Composition by Weight	Melting Point, °C
27% BeO, 73% Al_2O_3	1865
14% BeO, 86% Al_2O_3	1880
43% BeO, 57% MgO	1850
20% BeO, 80% ThO_2	2200
19% BeO, 81% ZrO_2	2240
35% BeO, 65% CaO	1450
28% BeO, 44% MgO, 28% Al_2O_3	1640
19% BeO, 39% Al_2O_3, 43% ZrO_2	1750
11% BeO, 48% Al_2O_3, 40% ThO_2	1810
18% BeO, 37% Al_2O_3, 45% ThO_2	1795
55% Al_2O_3, 45% ZrO_2	1885
61% Al_2O_3, 39% ThO_2	1910
85% ZrO_2, 17% CaO	2260
55% MgO, 45% Al_2O_3	2030
38% MgO, 62% SiO_2	1850
25% MgO, 75% ZrO_2	2250
75% ZrO_2, 25% SiO_2	2210

5. Carbides. The carbides are among the most stable of the solids, as several are believed to have softening points above 3500°C. They are hard, have fair thermal and electrical conductivity, but have only limited stability at high temperatures in air. In Table 64 are listed the available properties of the more stable carbides together with carbon itself.

Production of the Raw Material. Much literature is available on the production of the hard carbides for use in cutting tools. For example, tungsten carbide is made by grinding tungsten powder with 7 per cent carbon black and heated to 1600°C for 2 hr in a graphite container and cooled in an H_2 atmosphere. The cake contains 6.1 to 6.4 per cent combined carbon and 0 to 0.3 per cent free carbon. This material is wet ball milled in carbide mills to the desired size. Titanium carbide is made by adding 80 per cent of the theoretical carbon to titania, with TiO_2 or C added to correct the composition. This charge is then heated to 1900° C. Vanadium and neodymium carbides are made exactly like titanium carbide,

TABLE 63. PROPERTIES OF REFRACTORY OXIDES

Material	Formula	Sp gr g per CC	Hardness*	Tensile strength, M psi	Compressive strength, M psi	Young's modulus of elasticity, Mil. psi	Mp, °C	Bp, °C	Solubility[170]†
Aluminum oxide (α-alumina)	Al_2O_3 (101.92)	3.97[175]	9 M[168] 2000 K[178]	36 (20°C)[11] 33 (500°C) 18 (1200°C)	413 (20°C)[11] 70 (500°C) 20 (1200°C)	52 (20°C)[11] 50 (800°C) 32 (1400°C)	2050[168]	2980[175]	sl. s. H_2O, v. sl. s. a., alk.
Barium oxide..... (baria)	BaO (153.37)	5.72[168]	3.3 M				1923[168]	2200[175]	d. H_2O, s. H_2O, s. dil. a., al.; i. NH_3, acet.
Beryllium oxide.. (bromellite)	BeO (25.02)	3.00[175]	9 M[54] 1250 K[178]	14 (20°C)[11] 8 (500°C) 0.63 (1200°C)	103 (20°C)[11] 60 (500°C) 25 (1200°C)	45 (20°C)[11] 28 (800°C) 12 (1400°C)	2530 ± 30[172]	3900[175]	sl. s. H_2O; s. conc. H_2SO_4, fus. KOH; i. dil. a., alk.
Calcium oxide..... (lime)	CaO (56.08)	3.32[175]	4.5 M				2572[168]	2850[175]	d. H_2O, s. H_2O, s. a.
Cerium oxide..... (ceria)	CeO_2 (172.13)	7.13[175]	6 M				2600[175]		i. H_2O, s. H_2SO_4, HNO_3; i. dil. a.
Chromic oxide.	Cr_2O_3 (152.02)	5.21[168]					2435 ± 50[172]	3000[172]	i. H_2O, i. a., al., alk.
Cobalt oxide	CoO (74.94)	6.46[175]					1800[175]	3000[172]	i. H_2O, s. a., NH_4OH; i. al.
Columbium oxide...	Cb_2O_5 (265.82)	4.46[175]					1520[175]	2595[175]	
Ferric oxide ..... (hematite)	Fe_2O_3 (159.68)	5.20[175]	5.5–6 5 M[179]				1550[176]		i. H_2O, s. HCl
Gallium oxide.....	Ga_2O_3 (187.44)	6.44[170] 5.88					1740[175]		i. H_2O, s. h. a., alk.
Hafnium oxide.... (hafnia)	HfO_2 (210.6)	9.68[175]					2810[175]		i. H_2O
Lanthanum oxide. . (lanthia)	La_2O_3 (325.84)	6 51[168]					2320[175]	4200[175]	d. H_2O, s. H_2O, s. a, NH_4Cl; i. acet.
Lithium oxide..... (lithia)	Li_2O (29.88)	2.01[175]					1700[175]	1200[175] (600 mm)	d. H_2O, s. H_2O, s. acet., s. al., s. eth.
Magnesium oxide .. (periclase)	MgO (40.32)	3.58[175]	6 M[54]		112 (20°C)[183]	12 (20°C)[11]	2800[168]	2830[175]	sl. d H_2O; s. H_2O s. a., NH_4 salts: i. al.

Manganese oxide... (mangaosite)	MnO (70.93)	5.40[175]	5–6 M[179]				1785[175]		i. H_2O;s. a.,NH_4Cl
Nickel oxide..... (bunsenite)	NiO (74.69)	6.8[175]	5.5[179]				1990[172]		i. H_2O;s. a.,NH_4OH
Silicon oxide .... (high cristobalite)	SiO_2 (60.06)	2.32[168]	7 M[54] 820 K[178]				1728[175]	2920[175]	i. H_2O;s. HF;v. sl.s. alk.
Strontium oxide.... (strontia)	SrO (103.63)	4.7[168]	3.5 M				2430[168]	3000[175]	d. H_2O to $Sr(OH)_2$;sl. s. al.;i. eth.,acet.
Tantalum oxide.. .	Ta_2O_5 (441.76)	8.02[175]					1875[175]		i.H_2O;s. fus. $KHSO_4$;i. a.
Thorium oxide.... (thoria)	ThO_2 (264.12)	9.69[168]	6.5 M		220 (20°C)[11] 50 (500°C) 25 (1200°C)	21 (20°C)[11] 18 (800°C) 14 (1400°C)	3050[175]	4400[179]	i. H_2O;s. h. H_2SO_4;i, alk.,dil. a.
Tin oxide ..... (cassiterite)	SnO_2 (150.70)	7.00[175]	6–7 M				1825[175]	2227 d.[175]	i. H_2O;d. KOH,NaOH;i. aq. a.
Titanium oxide .. (rutile)	TiO_2 (79.90)	4.17[173]	5.5–6 5[179]				1830[175]		i. H_2O;s. H_2SO_4, alk.;i. a.
Tungsten oxide . (tungstite)	WO_3 (231.92)	7.16[178]					1473[168]	2460 d.[172]	i. H_2O,s. a.,KOH
Uranium oxide .	UO_2 (270.07)	10.75[175]					2280[175]		i. H_2O.s. HNO_3,conc. H_2SO_4
Vanadium oxide..	V_2O_3 (149.90)	4.87[168]					1970[164]		sl « H_2O,s. HNO_3,HF,alk.
Yttrium oxide. .... (yttria)	Y_2O_3 (225.84)	4.84[175]					2410[168]	4300[175]	s. H_2O,s. a.;i. alk.
Zinc oxide.. . . . (zincite)	ZnO (81.38)	5.66[175]	4–4.5 M[179]				1975 ± 25[172]	1720[175]	s. H_2O,s. min. a.,dil. ac. a.,NH_4OH
Zirconium oxide.... (zirconia)	ZrO_2 (123.22)	6.27[175]	6.5 M[179] 1160 K[183]	18 (20°C)[11]	303 (20°C)[11] 230 (500°C) 100 (1200°C)	36 (20°C)[11] 18 (800°C) 14 (1400°C)	2690 ± 20[172]	4300[179]	i. H_2O,s H_2SO_4,AF

* K = Knoop scale. M = Mohs scale.

† Explanation of abbreviations:

a. = acid
alk. = alkali
d. = decomposes
dil. = dilute
i. = insoluble
min. = mineral
s. = soluble
sl. = slightly
v. = very

TABLE 63. PROPERTIES OF REFRACTORY OXIDES (*Continued*)

Material	Sp heat, cal per g	Lin coef of therm exp, $\times 10^6$ °C	Coef of therm conductivity, Btu hr^{-1} ft^{-2} in. °F^{-1}	Resistivity, ohms per cc	$F_{298°K}$[137]	$H_{298°K}$[137]	$S_{298°K}$[137]	Solubility[179]†
Aluminum oxide (α-alumina)	0.21 (20°C)[11] 0.25 (500°C) 28 (1000°C)	6 (20°C)[11] 7 (500°C) 9 (1000°C)	17 (20°C)[11] 6 (500°C) 4 (1000°C)	2×10^{15} (100°C)[131] 3×10^{13} (300°C)	−365.9	−388.1	−74.58	sl. s. H_2O,v. sl. s. a., alk.
Barium oxide..... (baria)				1×10^{6} (300°C)[168] 2.2×10^{1} (500°C)				d. H_2O,s. H_2O,s.dil.a.,al.;i. NH_3,acet.
Beryllium oxide. (bromellite)	0.24 (20°C)[11] 0.50 (500°C)	8 (100°C)[74] 8 (500°C) 9 (1000°C)	10.4 (1200°C)	8×10^{13} (1000°C) 3.5×10^{10} (1600°C) 8×10^{8} (2100°C)	−132.0	−139.0	−23.42	sl.s. H_2O;s. conc. H_2SO_4,fus. KOH;i. dil. a.,alk.
Calcium oxide..... (lime)					−144.3	−151.7	−24.96	d. H_2O,s. H_2O,s. a.
Cerium oxide. ..... (ceria)		8.6 (500°C)[59]		2.2×10^{3} (800°C)[168] 1.9×10^{1} (1200°C)				i. H_2O,s. H_2SO_4, HNO_3,i. dil. a.
Chromic oxide		7 (500°C)[21] 12 (500°C)[57]		12.7×10^{2} (350°C)[168] 7.5×10^{1} (750°C)	−251.1	−270.6	−65.51	i. H_2O,i. a.,al.,alk.
Cobalt Oxide..					−176.8	−196.0		i. H_2O,s. a.,NH_4OH;i. al.
Columbium oxide .								
Ferric oxide..... (hematite)				3.6×10^{-2} (20°C)[168] 2.8×10^{-2} (200°C)	−179.1	−198.5	−65 0	i. H_2O;s. HCl
Gallium oxide....								ı H_2O,s. h. a.,alk.
Hafnium oxide... (hafnia)								i. H_2O
Lanthanum oxide . (lanthia)								d. H_2O,s. H_2O,s. a,NH_4Cl;i. acet.
Lithium oxide .... (lithia)						−9.6		d. H_2O,s. H_2O,s. acet.,s. al.,s. eth.
Magnesium oxide... (periclase)		11 (100°C)[11] 13 (500°C) 15 (1000°C)	36 (20°C)[11] 12 (500°C)	9×10^{12} (1000°C) 7×10^{9} (1600°C) 2×10^{8} (2100°C)	−138.43	−146.1	−25.73	sl. d.H_2O,s. H_2Os. a.,NH_4 salts; i. al.

Manganese oxide (mangaosite)	0.23 (20°C)[11] 0.26 (500°C) 0.28 (1000°C)				−87.8	−93.1	−17.73	i. H_2O,s. a.,NH_4Cl
Nickel oxide (bunsenite)				6.7×10^3 (600°C)[168] 1.4×10^2 (1000°C) 2.4×10^1 (1250°C)	−51.7	−58.4		i. H_2O,s. a.,NH_4OH
Silicon oxide (high cristobalite)				1×10^{15} (20°C) 7×10^6 (500°C)				i. H_2O;s. HF;v. sl.s. alk.
Strontium oxide (strontia)						−12.5		d. H_2O to $Sr(OH)_2$;sl. s. al.;i. eth.,acet.
Tantalum oxide								i.H_2O;s. fus. $KHSO_4$,l. a.
Thorium oxide (thoria)		8 (100°C)[71] 9 (500°C) 9 (1000°C)		4×10^{13} (20°C) 1.2×10^{12} (500°C)				i. H_2O;s. h. H_2SO_4;i,alk.,dil. a.
Tin oxide (cassiterite)		3.3 (500°C)[62]		6.6×10^3 (800°C)[168] 2.6×10^2 (1000°C) 1.0×10^1 (1300°C)				i. H_2O,d. KOH,NaOH,i. aq. a.
Titanium oxide (rutile)		7 (500°C)[71]		11.7×10^3 (900°C)[168] 7.5×10^3 (1000°C) 4.4×10^2 (1300°C)	−205.1	−218.0	−43.23	i. H_2O,s. H_2SO_4, alk.,i. a.
Tungsten oxide (tungstite)					−59.?	−66.6		i. H_2O,s. a.,KOH
Uranium oxide								i. H_2O,s. HNO_3,conc. H_2SO_4
Vanadium oxide					−294.0	−313.0	−64.04	sl. s. H_2O,s. HNO_3,HF,alk.
Yttrium oxide (yttria)								s. H_2O,s. a.,i. alk.
Zinc oxide (zincite)				6.7×10^3 (800°C)[168] 7.1×10^2 (1000°C) 5×10^0 (1350°C)	−76.5	−83.3		s. H_2O,s. min. a..dil. ac. a.,NH_4OH
Zirconium oxide (zirconia)	0.12 (20°C)[71] 0.16 (500°C)	11 (100°C)[11] 13 (500°C) 15 (1000°C)			−246.0	−258.8	−41.8	i. H_2O;s. H_2SO_4,AF

† Explanation of abbreviations:

a. = acid — aq. reg. = aqua regia — dil. = dilute — min. = mineral — sl. = slightly

alk. = alkali — d. = decomposes — i. = insoluble — s. = soluble — v. = very

TABLE 64. PROPERTIES OF REFRACTORY CARBIDES

Material	Formula	Sp gr, g per cc	Hardness*	Compressive strength, M psi	Mp, °C	Bp, °C	Solubility[179]†
Beryllium carbide...	Be_2C (30.03)	1.9[179]	2410 K[182]		2100 d.[179]		d. H_2O;s. a.
Boron carbide.. ..	B_4C (55.28)	2.51[183]	9 M 2800 K[179]	414 (20°C)[183]	2350[179]	3500[179]	i. H_2O;s. fus. alk.;i. a.
Calcium carbide.....	CaC_2 (64.07)	2.22[175]			2300[168]		d. to $ca(OH)_2 + C_2H_2$,not d. by conc.H_2SO_4
Cerium carbide.....	CeC_2 (292.26)	5.23[179]					d. H_2O;s. a.
Chromium carbide.....	Cr_3C_2 (180.03)	6.68[168]			1890[168]	3800[179]	ı. H_2O;s. dil. HCl
Columbium carbide...	CbC (104.91)				3497[180]		
Hafnium carbide.....	HfC (190.6)				4160[88]		
Iron carbide.....	Fe_3C (178.54)	7.4[168]			1837[168]		i. H_2O;s. a.
Lanthanum carbide....	LaC_2 (162.92)	5.02[179]					d. H_2O;s. H_2SO_4;i. conc. HNO_3
Lithium carbide.....	Li_2C_2 (36.98)	1.65			decom.[180]		d. H_2O;s. a.
Manganese carbide ..	Mn_3C (188.79)	6.89			1197[180]		d. H_2O:s. a.
Molybdenum carbide..	Mo_2C (203.91)	8.9[179]			2380[179]	4500[169]	
Silicon carbide.....	SiC (40.06)	3.17[168]	9–9.5 M 2550 K[184]	82 (20°C)[183]	2700[168]	2340[175]	i. H_2O;d. fus. KOH;i. a.
Tantalum carbide.....	TaC (192.89)				3880 ± 150[180]	5500[179]	i. H_2O;sl. s. H_2SO_4,HF
Thorium carbide.....	ThC_2 (256.14)	8.96[179]			2773[179]	5000[179]	d. H_2O;v. sl. s.conc. a.
Titanium carbide.....	TiC (59.91)	4.25[179]	8.9 M 2470 K[182]	109 (20°C)[183]	3140 ± 90[182]	4300[179]	i. H_2O;s. HNO_3,HNO_3 + HCl
Tungsten carbide.....	WC (195.93)	15.7[168]	1880 K[182]		2777[168]	6000[179]	i. H_2O
Uranium carbide.....	UC_2 (262.09)	11.28[168]			2400[168]	4100[179]	d.H_2O:s a
Vanadium carbide.....	VC (62.96)	5.4[168]	2080 K[182]	89 (20°C)[183]	2830[168]	3900[179]	i. H_2O;s. HNO_3,fus. KNO_3;i. HCl,H_2SO_4
Yttrium carbide.....	YC_2 (112.94)	4.13[179]					d. H_2O
Zirconium carbide. ...	ZrC (103.23)		2090 K[182]	23.8 (20°C)[183]	3530 ± 125[18]	5100[179]	i. H_2O;s. a..dil. HF

* K = Knoop scale; M = Mohs scale.

† See list of abbreviations, Table 63, pp 318–321.

TABLE 64. PROPERTIES OF REFRACTORY CARBIDES (*Continued*)

Material	Lin. coef. of therm. exp, °C × 10^6	Resistivity, ohms per cc	$F_{298°K}$ [156 180]	$H_{298°K}$ [156 180]	$S_{298°K}$ [156, 180]	Solubility [179]†
Beryllium carbide	12 (20°C) [183]	5 6 × 10^{-2} [183]				d. H_2O;s. a.
Boron carbide	4.5 (20–800°C) [183]	0.45 (20°C) 0.02 (500°C)				i. H_2O;s. fus. alk.;i. a.
Calcium carbide			−8.8	−7.0	+5.7	d. to ca$(OH)_2$ + C_2H_2;not d. by conc.H_2SO_4
Cerium carbide						d. H_2O;s. a.
Chromium carbide			−21.2	−21.0	+0.6	i. H_2O;s. dil. HCl
Columbium carbide						
Hafnium carbide						
Iron carbide			4.7	5.6	3.3	i. H_2O;s. a.
Lanthanum carbide						d. H_2O;s. H_2SO_4;i. conc. HNO_3
Lithium carbide				−27.8		d. H_2O;s. a.
Manganese carbide			−23.1	−23.0	−0.6	d. H_2O;s. a.
Molybdenum carbide			2.8	4.2	4.8	
Silicon carbide		0.5 (20°C)	−26.1	−26.7	−2.0	i. H_2O;d. fus. KOH;i. a.
Tantalum carbide						i. H_2O;sl. s. H_2SO_4,HF
Thorium carbide			−50.2	−45.6	+15.2	d. H_2O;v. sl. s.conc. a.
Titanium carbide			−56.5	−57.3	−2.2	i. H_2O;s. HNO_3,HNO_3 + HCl
Tungsten carbide					−1.7	i. H_2O
Uranium carbide			−3.4	−3.9		d. H_2O;s. a
Vanadium carbide		1.6 × 10^{-4} (20°C) [183]	−38	−36	−12	i. H_2O;s. HNO_3,fus. KNO_3;i. HCl,H_2SO_4
Yttrium carbide						d. H_2O
Zirconium carbide		5× 10^{-5} (20°C) [183]		−35.5		i. H_2O;s. a.,dil. HF

* K = Knoop scale; M = Mohs scale.

† See list of abbreviations, Table 63, pp. 318–321.

and molybdenum carbide is made in the same way as tungsten carbide.

Boron carbide, B_4C, is described in the paper of Ridgeway.[96] Its great hardness makes it of interest for gages, sand-blast nozzles, and polishing powder. It does not seem to be so resistant to oxidation as SiC. This material is made[11] from a mixture of boric acid and petroleum coke with 10 per cent excess boric acid to allow for volatilization. The mixture is melted in an arc furnace at about 2600°C. The product is ground in steel mills, acetone washed, and dried.

Silicon carbide is a well-known refractory, used for its high thermal conductivity, high resistance to spalling, and good resistance to slag attack. It is made in a resistance furnace as shown in Fig. 171. For example, a

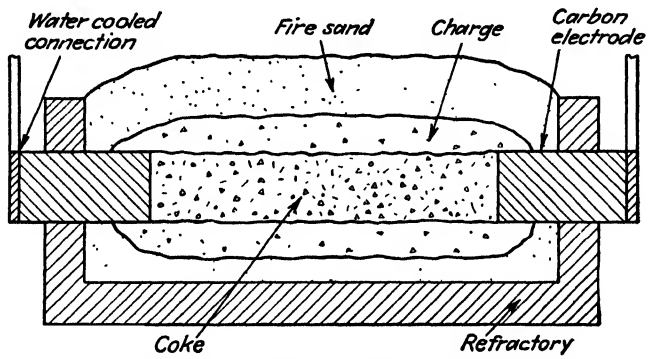


FIG. 171. Cross section of a silicon carbide furnace ready to start.

charge of 1,500 lb of petroleum coke, 9,000 lb of sand, 1,600 lb of sawdust, and 400 lb of salt is packed around the coke heater element, and this, in turn, is surrounded with low-grade SiC as an insulator. The furnace draws a maximum of 25,000 kw, reaches a temperature of 2200°C, and runs for about 36 hr. Perhaps 25 per cent of the charge is first-quality SiC. The power used is stated to amount to 4 to 5 kw-hr per lb.

Forming. The metal carbides may be formed by pressing the powder together with a few per cent of cobalt in steel or carbide dies at pressures up to 100,000 psi. Lubricants such as camphor, cetal alcohol, or waxes are used. The blocks are often fired or presintered in molybdenum resistance furnaces at 1050 to 1100°C for 2 hr in a hydrogen atmosphere. They are then sized and then sintered in a vacuum at 1500°C for 2 hr.

While it is difficult to obtain zero porosity in the carbides without using a permanent binder, such as 0.5 to 14 per cent cobalt, for refractory purposes, it should be possible to make pure dense articles by observing the principle described for the oxides and nitrides.

Many of the carbides can be formed by hot-pressing methods[183] (see Table 36, Chap. VIII). B_4C is especially adapted to this method and can be made into dense articles in graphite molds below 2375°C.

Silicon carbide is usually bonded with clay or phosphate but can be bonded by recrystallization, a process that is very costly because of the high temperature and long time needed.

Uses. Of course, the great use of the heavy metal carbides is for cutting tools and wear-resisting parts, where their hardness is the chief criterion. Silicon carbide, besides being a very valuable abrasive, is used largely as a refractory where high hot strength, good thermal conductivity, or resistance to slags are needed.

Carbides may also be of use for heaters and shields in high-frequency furnaces, as well as containers for reactions or melting.

It would, of course, be highly desirable if the carbide could be used in air at elevated temperatures. Silicon carbide, because of the viscous silica glass formed on the surface, is quite resistant to oxidation. There is much conflicting evidence as to the resistance of other carbides. Becker[86] states that Zr, Ti, and Hf carbides are the most resistant metal carbides, but no quantitative data are given. Hummel and Henry[72] state that TiC at 1100°C for 1 hr showed only surface alteration. Henry[73] states that B_4C oxidizes about ten times as rapidly as SiC. Beryllium carbide is also believed quite stable, but much more research is needed to get the facts.

6. Nitrides. The nitrides are more stable at elevated temperatures than is generally appreciated and are, therefore, of considerable interest where heating is not in air. Table 65 gives the available data on the more stable compositions from various references in the literature. It will be seen that several are believed to have melting points of over 3000°C.[111,113,116,123,124]

Titanium nitride can be formed from the tetrachloride by the following reactions:

$$TiCl_4 + XNH_3 \rightarrow TiCl_4 \cdot XNH_3$$
$$TiCl_4 \cdot XNH_3 \rightarrow TiN + 4NH_4Cl + H_2 + \tfrac{1}{2}N_2 + (X - 6)NH_3$$

Also it can be made from the oxide as follows:

$$TiO_2 + 2CaH_2 \rightarrow TiH_2 + 2CaO + H_2$$
$$TiH_2 \rightarrow Ti \text{ (finely divided)} + H_2$$
$$Ti \text{ (finely divided)} + NH_3 \rightarrow TiN + \tfrac{3}{2}H_2$$

The latter method is simpler and gives a product conforming more closely to the theoretical analysis of 77.4 per cent Ti and 22.6 per cent N. This material is the color of pure gold and shows no tarnish after long exposure.

Zirconium nitride can be prepared in the same way as TiN. It is also stable in air and has the appearance of green gold.

TABLE 65. PROPERTIES OF REFRACTORY NITRIDES

Material	Formula	Sp gr, g per cc	Mp, °C	Bp, °C	$F_{298°K}$[186,188]	$H_{298°K}$[186,188]	$S_{298°K}$[186,188]	Solubility[179]*
Aluminum nitride	AlN (40.98)	3.05[179]	2200 d.[179]	2200 d.[179]	−56.3	−64.0	−25.8	d. ev. NH_3;d. a.,al.
Barium nitride	Ba_3N_2 (438.08)		2200	2240 d.[179]	−72.9	−89.9	−57.4	
Beryllium nitride	Be_3N_2 (55.08)		2200[168]	2240 d.[17.]	−121.4	−133.5	−40.6	d. H_2O;a.,conc.alk.;i. a.
Boron nitride	BN (24.83)	2.25[179]	2730[179]	sub.[179]	−29.7	−33.5	−12.9	i. H_2O;d. HCl,HF,H_2SO_4
Cerium nitride	CeN (154.13)				−70.6	−78.8	−25.0	d. H_2O
Chromium nitride	CrN (66.02)		1770 d.[180]					i. H_2O;i. a.,alk.
Columbium nitride	CbN (106.92)	8.4[179]	2050 d.[179]		−53.0	−59.0	−20.0	s. HF + HNO_3;i. HNO.
Hafnium nitride	HN (192.6)		3300[180]		−72.0	−78.3	−22.0	
Lanthanum nitride	LaN (152.92)				−64.7	−72.1	−25.0	d.H_2O
Magnesium nitride	Mg_3N_2 (100.98)		1500 d.[179]		−96.2	−110.2	−47.2	i. H_2O(d.);s. a.;d. al.
Molybdenum nitride	Mo_2N (205.90)				−10.3	−16.6	−21.0	
Silicon nitride	Si_3N_4 (140.21)	3.44[179]	2170 sub.[180]	1900[180]	−154.7	−179.3	−81.6	i. H_2O;s. HF;i. a.
Scandium nitride	ScN (59 10)		2650[180]		−60.5	−68.0	−25.0	d. H_2O
Tantalum nitride	TaN (194.89)		3360[179]		−52.2	−58.1	−19.9	i. H_2O
Thorium nitride	Th_3N_4 (152.39)		2100[180]		−283.7	−310.4	−79.6	d. H_2O;s. a.
Titanium nitride	TiN (61.91)	5.29[179]	2900[180]		−73.5	−80.3	−22.9	i. H_2O;i. a.;s. aq.reg., alk.
Uranium nitride	U_2N_3 (770.24)	10.09[179]			−192	−213	−63	d. H_2O;s. HNO_3;i. conc. HCl,H_2SO_4
Vanadium nitride	VN (64.96)	5.63[168]	2050[168]		−34.5	−40.8	−21.0	i. H_2O
Zirconium nitride	ZrN (105.22)		2950[180]		−75.3	−82.2	−23.2	

* See list of abbreviations, Table 63, pp. 318–321

Boron nitride, according to Dr. Ryschkewitsch,[7] is produced from a mixture of lampblack and borax by the following reaction:

$$Na_2B_4O_7 + 2N_2 + 7C = 2Na + 7CO + 4\ BN$$
at temperatures as low as 1400°C

A white powder results much like talc or white graphite, which is quite stable in air.

Thorium nitride[124] can be formed in the same way as TiN, but it is difficult to approach the theoretical amount of nitrogen of 10.8 per cent.

The nitrides of cerium and lanthanum can be readily made; but as they hydrolyze rapidly in the atmosphere, they are of no great interest at present.

Beryllium nitride is readily formed by allowing the metal to react with NH_3 at 1000°C in a quartz tube, giving close to the composition represented by Be_3N_2.

Tantalum and vanadium nitrides can be formed by heating the metal in a stream of pure NH_3.

Forming. The grinding of the nitrides without contamination is somewhat of a problem, but the TiN and ZrN can be ground in steel ball mills and then acid washed. In other cases, grinding can be done in boron carbide mills with little contamination.

The powdered nitrides can be slip cast from water or absolute alcohol suspensions, or they can be pressed with a suitable temporary binder as described for beryllia. By proper sizing, pressing, and firing in ammonia, it is possible to produce nonporous ware. As the nitrides in general are electrical conductors, they can be heated in a high-frequency induction furnace directly.

Uses. The nitrides will find most use as a high-temperature refractory in a vacuum, especially for melting metals without contamination.

7. Sulfides. As sulfur comes next to oxygen in the Periodic Table, it might be thought that sulfides would have the high stability of oxides. There are many stable sulfides, such as CeS, ThS, US, and others as given by Brewer[180] in Table 66. However, it should be mentioned that none of them can be heated to elevated temperatures in air, owing to their rapid oxidation; but for work in high vacua and neutral atmospheres, these materials are very encouraging because of their low vapor pressures.

More specifically, Pauling[143] states that the sulfides of cerium and thorium, ThS and CeS, as well as related sulfides, have been found valuable as refractory materials. Previously, the lower sulfides were not known, and their initial production was due to the work of Drs. L. Brewer and E. D. Eastman and associates at the University of California. As an example of sulfide preparation, the formation of uranium sulfide will be described.[142]

Preparation of Sulfides. Three methods of preparation for the sulfides of uranium will be described below. By these methods pure US, U_2S_3, and US_2 have been prepared and other compositions may be prepared similarly.

Method 1

Step A. US_2 and intermediate sulfides all the way down to U_2S_3 may be prepared by treatment of the oxides, UO_2 or U_3O_8, with H_2S in a carbon system, followed by Step *B*, a vacuum heating, in the case of an intermediate sulfide. The temperature of reaction is 1200 to 1300°C, the rate of reaction at these temperatures being fairly rapid. During the course of the reaction, UOS is first

TABLE 66. SULFIDES[180]

Sulfide	$F_{298°K}$	$H_{298°K}$	$S_{298°K}$	Mp, °C	Sol.*	Volatility
MgS	−92.5	−71	(−23.7)	2000	d. H_2O	
CaS	−121.9	−128.9	(−23.7)		d. H_2O	
SrS	−121.6	−128.6	(−23.7)	2000	d. H_2O	
BaS	−119.7	−126.7	(−23.7)	2200	d. H_2O	
BeS	−65	−71	(−23.7)		d. H_2O	
⅓ La_2S_3	−107.2	−114	(−23.6)		i. H_2O	
CeS		−133.4		2450	i. H_2O	Rapid at 2200°C Slow at 1700°C
¼ Ce_3S_4		−120.9		2050	i. H_2O	
⅜ Ce_2S_3		−115.7		1900	i. H_2O	Slow at 1700°C
⅓ Nd_2S_3		−114			i. H_2O	
ThS		(−135)		2200	i. H_2O; sa	Moderate at 2200°C
⅓ Th_2S_3		(−125)		2000	i. H_2O; sa	Nonvolatile at 1700°C
⅐ Th_4S_7		(−114)		2000	i. H_2O; sa	Nonvolatile at 1700°C
½ ThS_2		(−106)		1900	i. H_2O; sa	
US				2000	s. dil. a	Rapid at 2200°C

* See list of abbreviations, Table 63, pp. 318-321.

formed at lower temperatures with the liberation of H_2O. As the temperature is raised to the maximum value, the H_2S being introduced attacks the carbon-producing CS, which then reacts with UOS, producing CO.

Because of the instability of US_2 at high temperatures, the product of reaction at high temperatures will be somewhat reduced to a lower composition, the extent of reduction depending upon the actual temperature. To insure formation of US_2 after all oxygen has been removed, the final reaction temperature will have to be lowered to below 1000°K, thus allowing the reduced sulfide to pick up sulfur from the H_2S.

Step B. The preparation of U_2S_3 and sulfides between US_2 and US is quite simple because of the US_2 instability. A sample of US_2 heated for 20 min at 1600°C in a vacuum of about 10^{-4} mm Hg is reduced to $US_{1.50}$, indicating the ease of reduction. $US_{1.6}$ heated at 1800°C dissociated to $US_{1.35}$ in 15 min. See US_{2-x} for further detail.

Method 2

When pure metal is available, any of the oxidation states of uranium can be prepared by action of the correct amount of H_2S upon the hydride prepared from the pure metal. The preparation of the hydride of uranium is conducted in a well-degassed bulb using pure hydrogen at a temperature of 300°C, the product of reaction being a finely divided powder ideal for reaction with a gas. A controlled amount of H_2S is then reacted with the hydride at 400 to 500°C, in a circulatory system which brings unreacted H_2S continually back over the sample until the required amount of H_2S has reacted. All products of this reaction including US_2 are not stable in air because of the low temperature of production, thus requiring handling in an inert atmosphere. If sulfides below US_2 are being produced, the product of the H_2S reaction will contain finely divided metal as well as a small amount of undecomposed hydride, and an additional heating at a higher temperature is thus necessary to obtain a uniform product. The US may be heated to above 1800°C to obtain a uniform product, while the U_2S_3 and higher sulfides must be heated for longer times at much lower temperatures to avoid loss of sulfur.

Method 3

Pure US_2 and uranium hydride may be mixed in the proper proportions to give the desired composition of product. Since the preparation procedures for the sulfide and hydride have been described above, no further comment is necessary. The hydride present in this mixture must first be decomposed to the metal, which is done in a vacuum at 400 to 600°C, after which the mixture is heated at a higher temperature to bring about complete interaction. This last step must be done at the proper temperature to avoid decomposition of the product through sulfur loss. This method is not usually satisfactory for composition between U_2S_3 and US_2 unless carefully carried out because of sulfur loss.

US_2. When pure metal is available, this sulfide may be prepared most simply through use of Method 2, since the apparatus may be constructed quite easily. The product from this procedure is less stable in air than that obtained through use of Method 1, however, because of the larger crystal form that results from the higher temperature treatment in the latter method. One advantage of Method 1 over Method 2 is that oxygen impurity is removed during the preparation, which is not the case during the low-temperature reaction of H_2S with the hydride which may contain oxygen.

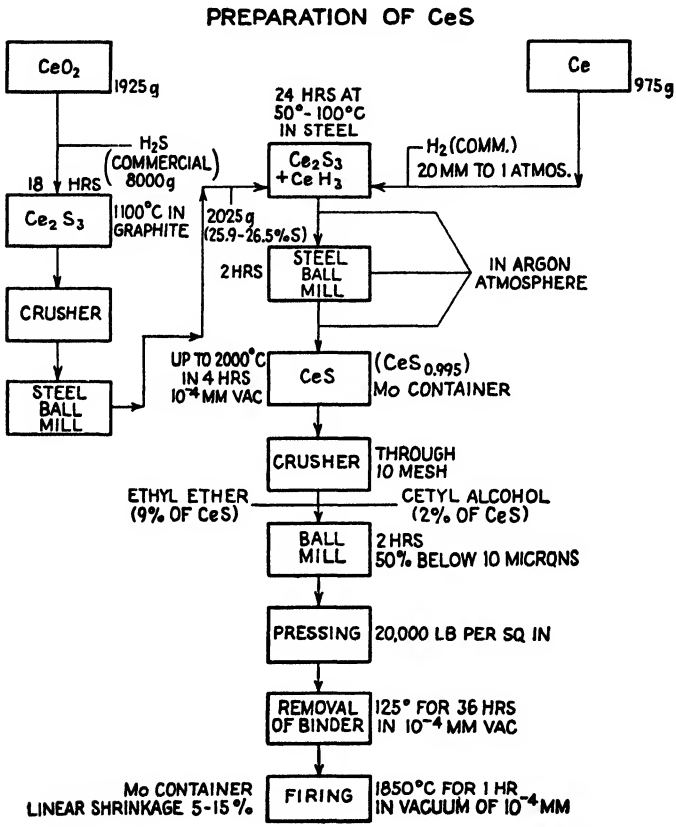
US_{2-x}. Intermediate compositions between US_2 and U_2S_3 are difficult to prepare by Method 3, since during the vacuum heating, considerable sulfur is lost from the starting US_2 during the dehydriding and from the final melt. If the composition does not have to be fixed closely, Method 1, Step *B*, is most convenient. If only a small number of samples are to be made, Method 2 is very convenient and the composition can be fixed more closely than by any of the other methods.

In the discussion of Method 1, Step *B*, it was stated that $US_{1.6}$ was reduced to $US_{1.35}$ by heating to 1800°C for 15 min. It should be stated that the original

mixture consisted of U and US_2 with a total composition of $US_{1.6}$ and the reduction to $US_{1.35}$ may be due to loss of sulfur from US_2 before reduction with the U. We have no evidence to indicate that reduction below U_2S_3 can be obtained by vacuum heating at this temperature.

US, the monosulfide, can be best prepared through use of either Method 3 or Method 2 with a subsequent treatment at a high temperature to obtain a uniform product.

TABLE 66*a*. FLOW SHEET FOR THE PREPARATION OF CERIUM SULFIDE



Physical and Chemical Properties of Uranium Sulfide. The monosulfide of uranium is a grayish, metallic-looking solid melting considerably above 2000°C. Like ThS, the crystal structure is cubic with a unit cell dimension determined by Zachariasen, of 5.473 Å. The calculated density based on the X-ray structure analysis is 10.87. In dilute acid the US is very slowly soluble. The magnetic susceptibility is $4180°10^{-6}$ emu.

CeS can be prepared from the sesquisulfide by the following reaction suggested by Brewer:

$$2CeH_3 + 2Ce_2S_3 = 6CeS + 3H_2$$

In this reaction, it is possible to control the ratio of Ce to S in the final product. The production of CeS from the oxide and metal is given in the flow sheet of Table 66*a* and the analyses of the materials in Table 66*b*.

TABLE 66*b*

Constituent	Material		
	Cerium oxide lindsay light optical grade	Cerium metal	Cerium sesquisulfide
CeO_2	89.4		
Ce		97.3	68.1
Ca	1.93	0.09	1.17
Mg	0.77	0.08	0.15
P	0.22		0.01
C		0.12	
Si	0.07		0.02
Pb	0.07		0.01
Fe	0.03		0.03
S			26.2
Ig. Loss	1.01		
Other R.E.	7.96	2.5	

Crucibles can be formed by pressing in steel molds in the same way as described for oxides. CeS has a metallic gold color and is quite stable in air. It has a density of 5.1 to 5.8 g per cc and a porosity of 0 to 10 per cent. The melting point is above 2200°C, and it thus makes an excellent container for vacuum melting of metals where freedom from oxygen is essential.

ThS is produced in substantially the same way. It is silvery in color with a density of 9.6 g per cc.

8. Borides. Little is known about the stable borides, but some data are shown in Table 69, Chap. XIII. HfB, WB_6, ZrB_3, BC_4, and NB are believed to have high melting points and low vapor pressures. Undoubtedly additional stable borides exist. NB and B_4C have been described in previous sections of this chapter, and little is known about the others. This is an interesting field of research.

9. Refractory Selenides, Silicides, and Phosphides. Very little is known of the compounds of these nonmetallic elements, but there is the possibility of some stable ones at high temperatures.

Brewer[180] records VSi_2 as melting at 1650°C and Ba_3P_2 with a melting point of 3200°C.

10. Refractory Single Crystals. The development of the lower melting crystals, such as the chlorides and fluorides, during the Second World War was brought to a high state of perfection by Dr. D. C. Stockbarger[144,147] and his associates at the Massachusetts Institute of Technology. However, when temperatures above the useful range of platinum are required, other methods have been developed.

Quartz. During the Second World War, considerable effort was made in Germany to produce synthetic quartz crystals for piezoelectric uses, as their supply of natural crystals was greatly curtailed. In general, two methods may be used to produce quartz: (1) by cooling a siliceous melt containing a mineralizer such as sodium tungstate and (2) by crystallization from a water solution at high temperatures. Sosman[145] mentions a number of methods on page IV 51. Along the same lines, the growing of quartz from SiO_2 dissolved in water that had been acidified by CO_2 and held at 320°C in a pressure vessel was mentioned by Norton.[148]

Nacken claims to have grown quartz crystals in the silver-lined autoclave shown in Fig. 172, where the amorphous quartz dissolves at the higher temperature and grows on the seed crystal suspended by a hair at a lower temperature. On the whole, it would seem that few if any quartz crystals of commercial size were made, as much effort was spent on substitutes.

Silverman[155] states that one of our glass companies has grown quartz crystals up to ½ in. on a side by dissolving silica glass (up to 3 per cent) in water at 350°C and then allowing precipitation onto a seed crystal by the foregoing method. The process goes on, as crystal quartz is said to be soluble to only 0.3 per cent under these conditions.

Corundum crystals with or without coloring oxides (sapphires or rubies) have been made for many years by building up a single boule with fine globules of melted alumina passing through an oxyacetylene flame by the well-known Verneuil process. An excellent description is contained in the report by Barnes.[151] Recently the Linde Air Products Company[154] has developed a method of growing single crystals of alumina in the form of rods, which can then be cut up for instrument jewels or ball-bearing balls. These rods are also of value in high-temperature expansion furnaces, as they have a much higher use limit than fused silica. Another use developed in the Ceramic Laboratories at the Massachusetts Institute of Technology consists in forming parts of an optical system of sapphires that are used inside a furnace up to 1500°C. A ruby color may be imparted to the crystal by adding about 0.5 per cent Cr_2O_3 to the alumina.

Spinel. Boules and rods of single crystals of spinel ($MgAl_2O_4$) are regularly made in various colors.[151,154] A hardening process used in Germany is described by Barnes[151] consisting of an unmixing with a deposite of fine Al_2O_3 crystals through the mass.

Beryls and Emeralds. Nacken is said to have made excellent beryls and emeralds by hydrothermal methods in a time of 3 or 4 days, using the

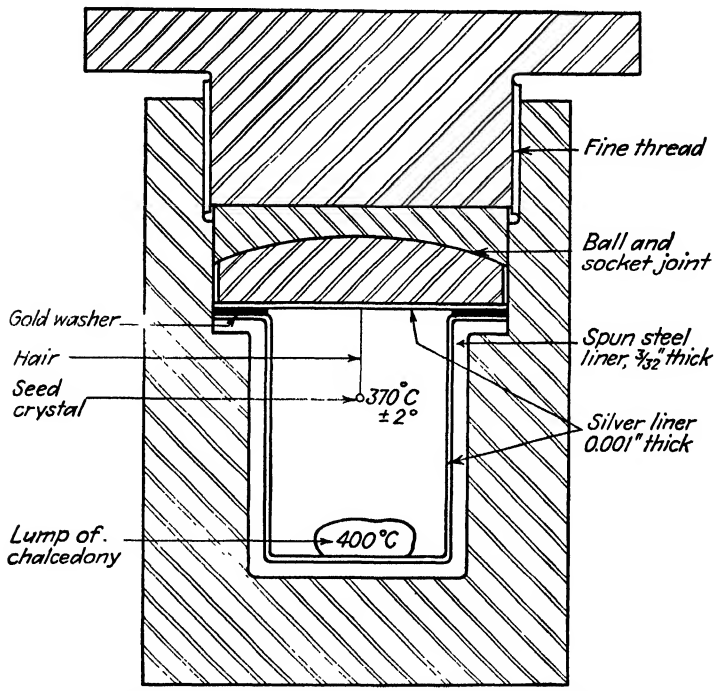


FIG. 172. Autoclave for growing synthetic crystals.

autoclave shown in Fig. 172. It is reported that very fine emeralds are being made in this country by much the same method.

Rutile. Single crystals of rutile (TiO_2) have been grown to fairly large sizes in the same way as for sapphires by the National Lead Company and the Linde Air Products Company. The high index of refraction of this stone, 2.8, gives it great brilliance as a gem and valuable optical and electrical properties.

Mica. While mica is not strictly a refractory material, its production is an important high-temperature problem as supplies of natural mica become exhausted. Considerable efforts have been made to produce it in Germany by Siemans and Halske and by Dr. Dietzel at Ostheim.[150] The

crystals are grown from a slowly cooled melt and from the composition would seem to be a fluorine mica, and not muscovite, as all the OH^- groups are replaced by F^-. It would seem impossible to grow muscovite outside hydrothermal conditions. Dietzel mentions the use of a magnetic field to orient the growing crystal, but there is considerable doubt as to its effectiveness. We have not as yet seen direct evidence of any large mica crystals grown in the laboratory.

It is reported that excellent tourmalines (a complex aluminum borosilicate) have been made in the laboratory.

11. Heterogeneous Refractory Systems. We have considered previously rather simple mixture of oxides with each other, but it is quite possible to mix, for example, metals and oxides. Such combinations are not new, as for many years platinum and porcelain[159] have been fired together to make a conducting body for electrodes, graphite and copper mixture is commonly used for motor brushes, cobalt is used to bond the hard carbides, and clay and graphite crucibles are extensively used for metal melting.

Much work has been carried out recently to produce bodies of good heat-shock resistance for gas turbine parts. For example, finely precipitated metallic iron and alumina[56,61] are fired together to give a body with excellent heat-shock resistance, but little is known of its creep values or its resistance to oxidation. Silicon carbide bonded with clay or a porcelain has been used for many years and is known to have an excellent heat-shock resistance and fair resistance to oxidation, but its creep value has not been published. Other suggested combinations are SiC–Cr, SiC–Si, Al_2O_3–Ni, Al_2O_3–Co. As yet we are not able to say whether or not any of these heterogeneous mixtures will be of value as refractories, but undoubtedly there is enough promise to warrant a basic study of this field.

Another type of system is the solid solution, such as TiC–TiO or US–UO_2. Little work has been done on such systems, but they certainly warrant more extensive study.

12. Refractory Glasses. The structure of glass is a random network of atoms in contradiction to the orderly placing of the atoms in the crystal lattice and may be thought of as an undercooled liquid. Glass is found to a small extent in nearly all of our refractories containing silica and serves a useful purpose in cementing the crystalline material together. On the other hand, for high use limits it is disadvantageous, for it causes flow under stress.

There has always been a demand for high-temperature glasses as containing vessels for vacuum furnaces, gas discharge lamps, and many other purposes where transparency is required, but as yet nothing of higher use limit than fused silica has been developed commercially.

Fused Silica. This glass is well known and generally used for high-temperature installations, but its use limit is about 1000°C due to devitrification. Because of its high viscosity, it must be worked at high temperatures and therefore is much more costly than the lower temperature glasses. The Nieder method[166] produces very clear material from powdered crystals.

Vycor. This glass is a unique development of the composition shown in Table 67. It is made from a soft glass that separates into two phases, one high in silica and the other high in borates. The latter is leached out, and the resulting siliceous framework shrunk by heating into a homogeneous structure much in the same way that porcelain is fired. For many purposes, it may replace the more costly fused silica.

High-alumina Glasses. For use in high-intensity gas discharge lamps, high-alumina glasses have been developed with a relatively high softening temperature and at the same time a reasonable temperature of melting. This is shown by the viscosity values from the Adams[162] patent in Table 68.

TABLE 67. COMPOSITION OF SOME HIGH-TEMPERATURE GLASSES

Constituent	Fused[162] silica	Vycor[162] glass	Pyrex[162] glass	High-alumina glass (*A*)	High-alumina glass (*B*)	Glass for sodium-vapor lamps[162]	Glass for tungsten seals[162]		Glass for molybdenum seals[162]
SiO_2	100	96.3	80.0	51.0	43.6	21.5	88.3	77.0	71.2
B_2O_3		2.9	12.0	1.6	11.3	40.0	8.4	15.4	14.6
Al_2O_3		0.4	3.0	20.0	20.4	22.0	2.9	1.0	2.4
Fe_2O_3			0.1					0.1	0.1
ZnO					10.1				
CaO				15.4	14.6		0.4	0.4	2.9
MgO				6.5		10.0			
BaO				0.5					
Na_2O		0.02	3.9			6.5		4.9	3.6
K_2O		0.02	0.3					1.9	4.0
Soft point, °C				918	840				

TABLE 68. VISCOSITY IN POISES

Temperature °C	Comm. soda-lime glass	Pyrex glass	High-alumina glass (*B*)
900	$10^{4.7}$	$10^{6.6}$	$10^{9.0}$
1000	$10^{3.9}$	$10^{5.6}$	$10^{6.5}$
1100	$10^{3.3}$	$10^{4.9}$	$10^{4.7}$
1200	$10^{2.8}$	$10^{4.3}$	$10^{3.5}$
1300	$10^{2.6}$	$10^{3.7}$	$10^{2.8}$

Metal Sealing Glasses. A number of high-silica glasses for sealing metals to fused silica—so-called graded seals—have been developed. A few are shown in Table 67.

Part III
PROPERTIES

CHAPTER XIII

THE FUSION POINT OF REFRACTORY MATERIALS AND THEIR EQUILIBRIUM DIAGRAMS

1. Fusion Process. At the present time, there is very little understanding of the mechanism concerning the fusing of nonmetallic materials. If a curve of viscosity is plotted against temperature, it will be found that for some materials, the change from a solid to a liquid occurs within a very small temperature interval whereas in other materials, especially silicates, the melting process is a more gradual one and occurs over a large temperature range. As shown earlier, it will be found, in the case of materials having a long softening range, that there is a great difference in the bond strength between the various atoms. For example, in the silicates, the bond strength that holds the silicon in the center of an oxygen tetrahedron is very strong and probably will not break up until much higher temperatures are reached than are necessary to break the weaker bonds. Therefore, we may conceive that when a silicate fuses, at first the weaker bonds are broken and a very viscous liquid results, which contains aggregates of the silicon-oxygen groups. As the temperature goes higher, these groups are broken up by the thermal agitation until the viscosity markedly decreases. Unfortunately, we have no experimental evidence to show just what happens in this process and can merely conjecture a mechanism that most nearly fits the facts.

In the literature, it will be found that the terms "melting point," "softening point," and "fusion point" are used more or less indiscriminately in discussing refractories. The best usage would seem to indicate that the term melting point should be reserved for pure materials and fusion or softening point for more complex or impure materials. It is, of course, difficult to draw a sharp boundary between the two; so it was thought best to use the term fusion point throughout this chapter for everything except the pure materials, as the majority of the refractories show a considerable softening range.

2. Method of Obtaining Fusion Points. *Physical Significance of the Fusion Point.* There has been a great deal of confusion in considering just what is meant by the fusion point of the average refractory. We can do no better than refer to the method used by the glass technologist in determining the fusion or softening point of glass. Here, the fusion point

is specified as the temperature at which the particular specimen under a definite stress becomes sufficiently fluid to flow at a specified rate. No other meaning will have any significance in discussing materials that have no sharp boundary between the solid and liquid state.

This definition of fusion point can be made clear by the curve in Fig. 173 in which the deformation in millimeters of the specimen is plotted against the time, under the conditions where the specimen is heated up at a uniform rate. If we are arbitrarily assuming the fusion point as that temperature at which the rate of flow equals 0.01 mm per sec, a tangent can be drawn to the flow curve with this slope. The point where the curve and tangent meet will represent the fusion temperature, which, in the illustration, is 3143°F. Owing to experimental difficulties, the usual methods of measuring the fusion points do not follow such an exact procedure; consequently, only an approximate value is obtained.

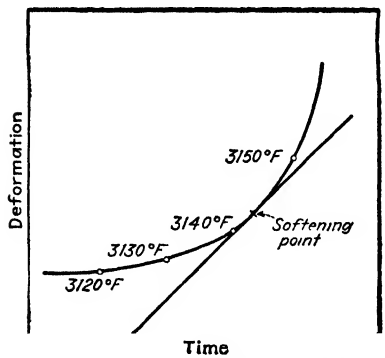


FIG. 173. Method of determining the softening point.

Determination of Fusion Points by Comparison with the Pyrometric Cones. A common method of determining the fusion point is by comparing the bending characteristics of the sample with those of a series of standard pyrometric cones all run in the same furnace. As it can be carried out by persons not skilled in pyrometric practice and with inexpensive equipment, this method has the advantage of simplicity. It has the disadvantage, however, of not giving the highest degree of precision, because of variations in the furnace atmosphere or from other causes that are not easy to control. Under good conditions, however, a precision of ± 15°C (27°F) should be obtained. The following quotation gives the standard ASTM softening-point test for refractory materials:

STANDARD METHOD OF TEST FOR PYROMETRIC CONE EQUIVALENT OF REFRACTORY MATERIALS

ASTM Designation C 24–42[1]

ADOPTED, 1920; REVISED, 1928, 1931, 1933, 1935, 1942, 1946

The Standard of the American Society for Testing Materials is issued under the fixed designation C 24; the final number indicates the year of original adoption as standard or, in case of revision, the year of the last revision.

[1] ASTM Standards are subject to revision. The Society's headquarters, in Philadelphia, may be consulted for the latest information.

1. Scope. This method is intended for determining the Pyrometric Cone Equivalent of fireclay, fireclay brick, silica cement, and ground fireclay by comparison of test cones with Standard Pyrometric Cones under the conditions herein prescribed.

2. Preparation of Sample. (*a*) *Clay or Brick.* The entire sample of fireclay or fireclay brick, in case the amount is small, shall be reduced in size by means of rolls or a jaw crusher to a maximum size of ¼ in. In case the amount is large, a representative sample obtained by approved methods shall be so treated. The sample shall then be mixed thoroughly, and the amount reduced to about 250 g (0.5 lb) by quartering. Any magnetic material introduced by crushing or grinding shall be removed by means of a magnet. This portion shall then be ground in an agate, porcelain, or hard steel mortar, and the amount reduced again by quartering. The final size of the sample shall be 50 g, and the fineness such that it will pass a No. 70 (210 μ) ASTM sieve (equivalent to mesh No. 65 of the Tyler standard series). In order to avoid excessive reduction of fines, they shall be removed frequently during the process of reduction by throwing the sample on the sieve and continuing the grinding of the coarser particles until all the sample will pass through the sieve.

b. Silica Cements. In the case of silica cements, the sample obtained by approved methods shall be tested as received without grinding or other treatment.

NOTE: For the purpose of this test, silica cement is understood to be the usual finely ground mixture of quartzite, silica brick, and fireclay of various proportions and does not include materials sold under the name of high-temperature mortars.

3. Preparation of Test Cones. *a.* The dried sample shall be thoroughly mixed and, after the addition of sufficient dextrin, glue, gum tragacanth, or other alkali-free organic binder and water, shall be formed in a truncated trigonal pyramid with its base at a small angle to the trigonal axis and of the following dimensions: over-all height (between planes perpendicular to the trigonal axis) 1⅛ in.; length of the side of the trigonal tip, 0.075 in.; length of the two longer sides of the base, $\frac{9}{32}$ in.; base at an external angle of 82 deg to one face and perpendicular to the symmetry plane through the opposite edge of the pyramid.

b. When dry, the test cones may be subjected, when necessary, to a preliminary burn at a temperature not exceeding 2370°F (1300°C) for the purpose of sintering them into a firm condition to permit handling.

4. Mounting. The test cones shall be mounted on plaques of refractory material of such a composition as will not affect the fusibility of the cones.* They shall be mounted with the base embedded approximately 3 mm (0.12 in.) in the plaque, and the face of one side inclined at an angle of 82 deg with the horizontal. The arrangement of the test cones with respect to the Standard Pyrometric Cones shall be substantially as shown in Fig. 174, *i.e.*, alternating the test cones with the Standard Pyrometric Cones in so far as practical (Note, p. 350). The plaque may be any convenient size and shape and may be biscuited before using, if desired.

* A mixture of equal parts of a highly refractory clay such as a good grade of china clay and fused alumina which will pass a No. 100 (149 μ) ASTM sieve (equivalent to mesh No. 100 of the Tyler standard series) has been found satisfactory.

NOTE: The number of cones and their mounting so as to face inward as shown in Fig. 174 is typical for gas-fired furnaces of relatively large dimensions and gases moving at high velocity. The practical bore of the muffle tubes in most electric furnaces does not permit cone pats of this size. The static atmosphere prevailing permits the cones being mounted to face outward, if so desired.

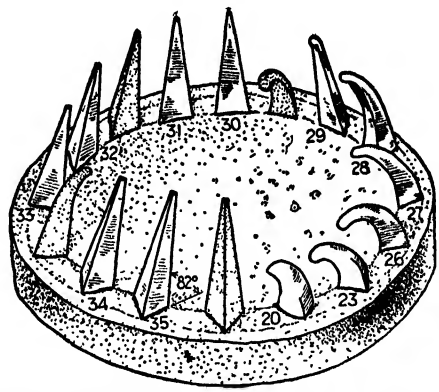


FIG. 174. Method of mounting test cones and appearance after testing.

5. Heating. *a.* The heating shall be carried out in a suitable furnace at a rate to conform to the following requirements:

	Minutes		Minutes
To reach cone No. 20	45	Time interval to:	
Time interval to:		Cone 32	8
Cone No. 23	20	Cone No. 32½	9
Cone No. 26	6	Cone No. 33	9
Cone No. 27	4	Cone No. 34	6
Cone No. 28	4	Cone No. 35	10
Cone No. 29	10	Cone No. 36	10
Cone No. 30	4	Cone No. 37	4
Cone No. 31	12	Cone No. 38	6

NOTE: At 1830°F (1000°C) the old cone pat may be removed and a new one put in without cooling the furnace down below red heat.

b. That type of furnace in which a neutral or oxidizing atmosphere may be maintained is to be preferred. Excessive reducing conditions should be avoided. Care should be taken that the flame does not strike directly against the cone or cone plaque. The furnace should be tested at intervals for the determination of the uniformity of the distribution of the heat.

6. Pyrometric Cone Equivalent. *a.* The softening of the cone will be indicated by the top bending over and the tips touching the plaque. The bloating, squatting or unequal fusion of small constituent particles should always be reported. The Pyrometric Cone Equipment shall be reported in terms of Standard Pyrometric Cones and shall be that cone which most nearly corresponds in time of softening

with the test cone. If the test cone softens later than one Standard Pyrometric Cone but earlier than the next Standard Pyrometric Cone and approximately midway between, the P.C.E. shall be reported thus: Cone No. 31–32.

b. If the test cone starts bending at an early cone but is not down until a later cone, the fact should be reported.

Determination of Fusion Points with the Optical Pyrometer. A more precise determination of the fusion point can be made with the optical pyrometer, which is sighted on the test specimen heated in a furnace under black-body conditions. With ordinary care, a precision of ±7°C (about 12.6°F) should be obtained; and with especial care in calibration, a precision of ±4°C (about 7.2°F) is possible.

Most of the fusion points have been made on specimens formed into a slender tetrahedron similar in shape to the standard pyrometric cone. This particular form of specimen has commonly been used because the bending can readily be seen without special measuring apparatus, but it does have certain disadvantages for precise work because (1) the size of the specimen varies, depending on the shrinkage of the refractory material; (2) the density of the specimen varies with the material so that the bending forces are variable; and (3) the bending forces vary with the position of the cone.

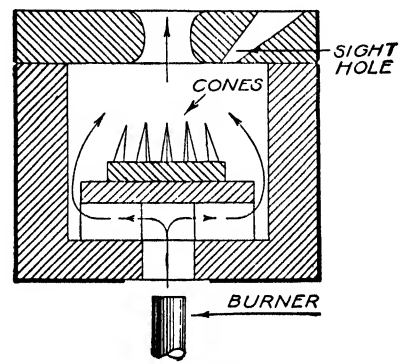


FIG. 175. A gas-fired fusion-point furnace.

Apparently a much better form of specimen for fusion-point tests would be a small bar supported at its ends. On heating, this bar will soften and sag in the middle. By sighting on the center of the bar with a reading telescope, it is possible to plot the amount of settling against time and thus obtain a curve capable of giving a precise value of fusion point as shown in Fig. 174. Certain precautions are necessary, however, in this type of test: (1) The material should be precalcined in order to shrink it to a stable volume, and (2) the distance between the supports should be so arranged as to give a definite stress in the specimen based on its density and cross-sectional area.

Furnaces for Determining Fusion Points. Fusion points can be determined in a cylindrical type of furnace heated by a gas and air burner up to temperatures of 1700°C (about 3090°F). Figure 175 shows such a furnace for determining fusion points in comparison with pyrometric cones. For higher temperatures, the same type of furnace can be used with oxygen

instead of air, in which case temperatures as high as 2000°C (about 3630°F) can be reached. The high-frequency induction furnaces shown in Chap. X are excellent for melting-point determinations.

Preparation of Fusion-point Specimens. In making up specimens for fusion-point determinations, it is essential that representative samples be taken. For example, if the fusion point of a brick is desired, the brick should be broken up and a number of random samples taken. These fragments are then ground so that they will completely pass a 65-mesh

FIG. 176. A riffle sampler. (*Courtesy of W. S. Tyler Company.*)

screen. Grinding should be carried out at first in a steel mortar; and if the material is very hard, iron specks should be removed with a magnet. The final grinding should be done in an agate mortar. In the case of clay, the usual sampling methods should be employed in order to ensure representative results. In the case of lump clay, such as bauxite, it will be found that the hard nodules have a higher melting point than soft material; therefore a considerable amount must be crushed and split down to a small sample. A riffle sampler such as that shown in Fig. 176 is excellent for the purpose.

The sample is moistened with water and pressed with a spatula into a mold. With nonplastic materials, an organic binder is used. It is usually desirable to make the cones small, as they will more readily follow the temperature of the furnace. A cone 1 in. high with a $\frac{3}{16}$-in. triangular

base, according to the standard of the American Society for Testing Materials, is very satisfactory. A mold for making these cones is shown in Fig. 177. Considerable manipulative skill is required to make and handle cones made from lean or sandy materials.

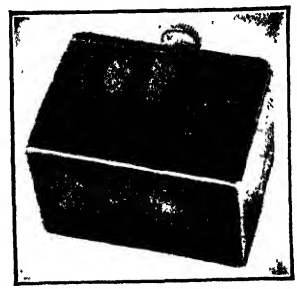


FIG. 177. A mold for making test cones.

The cones should be carefully dried before being placed in the melting furnace; and if they are fragile, they should be given sufficient preliminary heating to frit them together. In placing a cone on a boat, it is a good idea to cut a shallow recess and cement the base of the cone into it, but great care should be taken to make this cement out of the identical material from which the cone is made, as otherwise a reaction may occur that will give a fusion point considerably too low. In every case, the cone should be placed so that the face will make an angle of 82 deg with the horizontal, as shown in Figs. 178 and 179.

Effect of Atmosphere on Fusion Point. The fusion point of pure silica or alumina is little, if at all, influenced by the furnace atmosphere; however, when any impurity is present, especially iron oxide, the atmosphere does

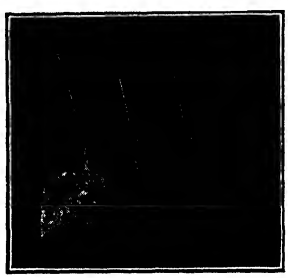


FIG. 178. Cones ready for placing in the kiln. (*Courtesy of The Standard Pyrometric Cone Company.*)

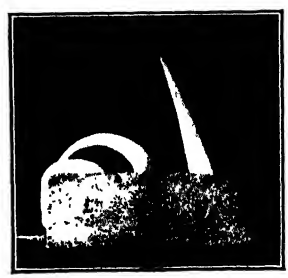


FIG. 179. Cones after firing. Cone 6 is just down. (*Courtesy of The Standard Pyrometric Cone Company.*)

have a marked effect on the fusion point. Just why the reduced oxide should combine more readily with the other constituents to form a low-melting compound is not known. Fieldner, Hall, and Feild[1] found that when the iron oxide in the mixture was reduced to the metallic condition below the softening temperature, little lowering of the fusion point resulted. Apparently the act of reduction makes the iron oxide more active in combining with the other constituents.

The influence of the atmosphere on the fusion point of fireclay containing very finely divided iron oxide is shown by the results of Vickers and

Theobald.[63] The effect of the reducing gases is very marked (Fig. 180) and shows that the lowering of the fusion point increases almost directly with the iron oxide content.

Test cones in a reducing atmosphere seldom bend over smoothly. Often a hard coating forms, allowing the molten center to run out at the

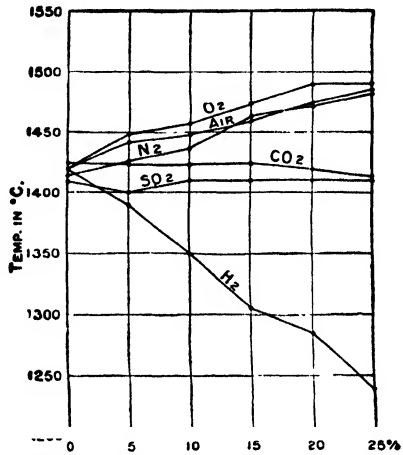


FIG. 180. Curves showing the fusion temperatures of a clay containing various proportions of finely divided ferric oxide in various gases.

base. Fusion points should be taken only when the test cone bends down gradually until the tip touches the base, as in *A* of Fig. 181. When a cone bends only at the base, as in *B*, it is probable that interaction has occurred between the cone and the plaque. Some materials even under the best conditions will not give good readings but will either bloat, *C*, or

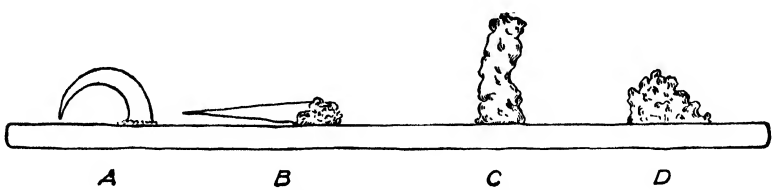


FIG. 181. Behavior of specimen cones on firing.

slump down, *D*. Unless for some special purpose, fusion points should always be made in an oxidizing or neutral atmosphere.

3. Fusion Point and Composition. A number of relations have been suggested to connect the chemical composition of a clay with its fusion point. Perhaps the earliest work on this subject was that of Richter, who showed that various fluxes had equal effects if they were taken in molecular equivalents; *i.e.*, 40 parts of MgO would have the same influence

on a clay as 94 parts of K_2O. He also stated that if a number of fluxes are present, their influence is proportional to the sum of their equivalents. We know now that these relations are not strictly true, but this work was a great step forward in logical procedure.

Richter's law has been applied to fireclay by Ludwig,[11] who found the law restricted to certain conditions, such as low concentrations and intimate mixtures.

Schuen[16] gives for the fusion point of a clay, in degrees centigrade, the following formula:

$$\frac{360 + Al_2O_3 - RO}{0.228}$$

The Al_2O_3 and RO are given in percentage weight, so calculated that the Al_2O_3 and SiO_2 equal 100. He finds that although this formula gives fair average results, there are many other important influences, such as grain size and state of oxidation.

H. Salmang[14] and Hohler[17] have studied the influence of grain size on the fusion point. They find that the finer the grain the lower the fusion value.

Many attempts have been made to correlate the atomic structure of a crystal with its melting point, for it should be possible to determine this value from the bond strengths in the lattice. Although certain correlations exist in some of the simple structures like a series of alkali halides, the structures are, in general, too complicated to handle directly. However, it is possible to formulate a few general rules from the data available.

In the first place, the only compounds having high fusion points are borides, carbides, nitrides, oxides, and sulfides. It is interesting to notice that the five elements boron, carbon, nitrogen, oxygen, and sulfur are adjacent to one another in the Periodic Table. Although we do not have particularly accurate values of fusion point for the high-temperature materials, it would seem reasonable to expect that the small number of electrons in the outer shell of this series correspond to the higher fusion point. There are few data on the melting point of the fluorides, and none listed goes above 1400°C (about 2550°F). It should be remembered that most of the nitrides, carbides, borides, and sulfides are unstable in an oxidizing atmosphere.

It will also be noticed that all the high-melting-point compounds have a valence number of 2 or over, and a general tendency indicates that the higher the ionic bonding the higher the fusion point. It may also be noted that many of the refractory materials have a high hardness, generally over 6, if we neglect the unstable materials containing the CO_2 or OH groups. Then again, the refractory materials generally have a high density, very

few being below 3.0. Although very few data are available, there is evidence to indicate that materials having the lowest volume compressibility are the most refractory, which would also follow from our conception of high bond strength.

4. Melting Point of Some Refractory Materials. Table 69 shows the melting points of pure refractory materials in so far as they are at present available, taken largely from the following phase diagrams. It should be realized that the determination of the fusion points of these very refractory materials presents great difficulties and that undoubtedly more refined work will alter many of them in the future. In fact, any value above 2000°C (about 3630°F) may be open to considerable error.

TABLE 69. MELTING POINTS OF PURE REFRACTORY MATERIALS

Elements

Material	Formula	Melting point	
		°C	°F
Boron	B	2300	4170
Columbium	Cb	1950	3540
Graphite	C	3700	6690
Hafnium	Hf	1700	3000
Iridium	Ir	2450	4440
Molybdenum	Mo	2630	4770
Osmium	Os	2700	4890
Platinum	Pt	1775	3240
Rhenium	Re	3000	5430
Rhodium	Rh	1966	3570
Ruthenium	Ru	2450	4440
Tantalum	Ta	3000	5430
Thorium	Th	1845	3350
Titanium	Ti	1800	3270
Tungsten	W	3410	6170
Vanadium	V	1710	3110
Zirconium	Zr	1800	3270

Oxides

Material	Mineral or common name	Formula	Melting point	
			°C	°F
Aluminum oxide	Alumina	Al_2O_3	2050	3720
Barium oxide		BaO	1923	3490
Beryllium oxide	Bromellite	BeO	2530	4580
Calcium oxide	Lime	CaO	2570	4660
Cerium oxide	Ceria	CeO_2	2600	4710
Chromium oxide		Cr_2O_3	2435	4410

TABLE 69. MELTING POINTS OF PURE REFRACTORY MATERIALS (*Continued*)
Oxides (*Continued*)

Material	Mineral or common name	Formula	Melting point	
			°C	°F
Cobalt oxide		CoO	1800	2370
Columbium oxide		Cb_2O_5	1520	2770
Gallium oxide		Ga_2O_3	1740	3160
Hafnium oxide	Hafnia	HfO_2	2810	5090
Lanthium oxide	Lanthia	La_2O_3	2320	4208
Lithium oxide	Lithia	LiO_2	1700	3090
Magnesium oxide	Periclase	MgO	2800	5070
Manganese oxide	Manganosite	MnO	1785	3250
Nickel oxide	Bunsenite	NiO	1990	3610
Silicon oxide	Cristobalite	SiO_2	1725	3130
Strontium oxide	Strontia	SrO	2430	4410
Tantalum oxide		Ta_2O_5	1875	3310
Thorium oxide	Thoria	ThO_2	3050	5520
Tin Oxide		SiO_2	1825	3320
Titanium oxide	Titania	TiO_2	1830	3330
Tungsten oxide		WO_3	1470	2680
Uranium oxide		UO_2	1970	3580
Vanadium oxide		V_2O_3	1970	3580
Yttrium oxide	Yttria	Yt_2O_3	2410	4370
Zinc oxide	Zincite	ZnO	1975	3590
Zirconium oxide	Zirconia	ZrO_2	2690	4870
	Silicates			
Aluminum silicate	Mullite	$3Al_2O_3 \cdot 2SiO_2$	1810*d*	3290*d*
Barium silicate	Metasilicate	$BaO \cdot SiO_2$	1605	2921
Barium silicate		$BaO \cdot SiO_2$	1420	2588
Barium silicate	Orthosilicate	$2BaO \cdot SiO_2$	>1755	>3191
Barium silicate		$2BaO \cdot 3SiO_2$	1450	2642
Barium aluminum silicate	Celsian	$BaO \cdot Al_2O_3 \cdot 2SiO_2$	>1700	>3092
Barium calcium silicate		$BaO \cdot 2CaO \cdot 3SiO_2$	1320*d*	2408
Barium zirconium silicate		$BaO \cdot ZrO_2 \cdot SiO_2$	1573	2864
Beryllium silicate	Metasilicate	$BeO \cdot SiO_2$	>1755	>3191
Beryllium silicate	Orthosilicate	$2BeO \cdot SiO_2$	2000	3632
Beryllium aluminum silicate	Beryl	$3BeO \cdot Al_2O_3 \cdot 6SiO_2$	1410	2570
Calcium silicate		$3CaO \cdot SiO_2$	1900	3452
Calcium silicate	Orthosilicate	$2CaO \cdot SiO_2$	2130	3866
Calcium silicate		$3CaO \cdot 2SiO_2$	1475	2687
Calcium silicate	Pseudowollostonite	$CaO \cdot SiO_2$	1540	2804
Calcium aluminum silicate	Anorthite	$CaO \cdot Al_2O_3 \cdot SiO_2$	1550	2822

TABLE 69. MELTING POINTS OF PURE REFRACTORY MATERIALS (*Continued*)
Silicates (*Continued*)

Material	Mineral or common name	Formula	Melting point °C	Melting point °F
Calcium aluminum silicate	Gehlenite	$2CaO \cdot Al_2O_3 \cdot SiO_2$	1590	2894
Calcium magnesium silicate	Monticellite	$CaO \cdot MgO \cdot SiO_2$	1498*d*	2728
Calcium potassium silicate		$CaO \cdot K_2O \cdot SiO_2$	1620	2948
Calcium zirconium silicate		$CaO \cdot ZrO_2 \cdot SiO_2$	1582	2880
Iron silicate	Gruenerite	$FeO \cdot SiO_2$	1550	2822
Magnesium silicate	Forsterite	$2MgO \cdot SiO_2$	1890	3434
Magnesium silicate	Clino-enstatite	$MgO \cdot SiO_2$	1557*d*	2835*d*
Magnesium zirconium silicate		$MgO \cdot ZrO_2 \cdot SiO_2$	1793	3260
Manganese silicate	Tephroite	$2MnO \cdot SiO_2$	1320*d*	2408*d*
Potassium aluminum silicate	Kaliophilite	$K_2O \cdot Al_2O_3 \cdot 2SiO_2$	1790	3254
Potassium aluminum silicate	Leucite	$K_2O \cdot Al_2O_3 \cdot 4SiO_2$	1810	3290
Silica	Cristobalite	SiO_2	1710	3110
Sodium zirconium silicate		$Na_2O \cdot ZrO_2 \cdot SiO_2$	1708	3107
Sodium aluminum silicate	Nephalite	$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$	1526	2779
Strontium silicate		$2SrO \cdot SiO_2$	>1700	>3092
Strontium silicate		$SrO \cdot SiO_2$	1580	2876
Strontium aluminum silicate		$SrO \cdot Al_2O_3 \cdot 2SiO_2$	>1700	>3092
Zinc silicate	Willemite	$2ZnO \cdot SiO_2$	1509	2748
Zinc zirconium silicate		$ZnO \cdot ZrO_2 \cdot SiO_2$	2078	3773
Zirconium silicate	Zircon	$ZrO_2 \cdot SiO_2$	2500	4532
Aluminates (Other Than Spinels)				
Calcium aluminate		$5CaO \cdot 3Al_2O_3$	1455	2651
Calcium aluminate		$3CaO \cdot 5Al_2O_3$	1720	3128
Calcium aluminate		$3CaO \cdot Al_2O_3$	1535*d*	2795
Calcium ferric aluminate		$4CaO \cdot Fe_2O_3 \cdot Al_2O_3$	1415	2579
Calcium sodium aluminate		$3CaO \cdot 2Na_2O \cdot 5Al_2O_3$	>1630	>2966
Calcium sodium aluminate		$8CaO \cdot Na_2O \cdot 3Al_2O_3$	1508*d*	2746*d*
Lithium aluminate		$Li_2O \cdot Al_2O_3$	>1625	>2957
Sodium aluminate		$Na_2O \cdot Al_2O_3$	1650	3002
Titanium aluminate		$TiO_2 \cdot Al_2O_3$	1860	3380

TABLE 69. MELTING POINTS OF PURE REFRACTORY MATERIALS (*Continued*)

Material	Mineral or common name	Formula	Melting point °C	Melting point °F
Nitrides				
Aluminum nitride		AlN	2200*d*	3990*d*
Barium nitride		Ba_3N_2	2200	3990
Beryllium nitride		Be_3N_2	2200	3990
Boron nitride		BN	2730	4950
Chromium nitride		CrN	1770*d*	3220*d*
Columbium nitride		CbN	2050*d*	3720*d*
Hafnium nitride		HfN	3300	5970
Magnesium nitride		Mg_3N_2	1500*d*	2730*d*
Silicon nitride		Si_3N	2170	3940
Scandium nitride		ScN	2650	4800
Tantalum nitride		TaN	3360	6080
Thorium nitride		Th_3N_4	2100	3810
Titanium nitride		TiN	2900	5250
Vanadium nitride		VN	2050	3720
Zirconium nitride		ZrN	2950	5340
Titanates				
Beryllium titanate		$3BeO \cdot TiO_2$	1810	3290
Beryllium titanate		$BeO \cdot TiO_2$	1720	3128
Calcium titanate		$CaO \cdot TiO_2$	1980	3596
Calcium titanate		$2CaO \cdot TiO_2$	1800	3272
Calcium titanate		$3CaO \cdot TiO_2$	1840	3344
Magnesium titanate		$2MgO \cdot TiO_2$	1830	3326
Magnesium titanate		$MgO \cdot 2TiO_2$	1670	3038
Manganese titanate	Pyrophanite	$MnO \cdot TiO_2$	1404	2559
Borides				
Boron nitride		NB	3000	5432
Hafnium boride		HfB	3065	5549
Iron boride		Fe_2B_5	1340	2444
Iron boride		Fe_5B_2	1351	2464
Tungsten boride		WB_6	2920	5288
Zirconium boride		ZrB_3	2990	5414
Carbides				
Beryllium carbide		Be_2C	2100*d*	3810
Boron carbide		B_4C	2350	4230
Calcium carbide		CaC_2	2300	4170
Chromium carbide		Cr_3C_2	1890	3430
Columbium carbide		CbC	3500	6330
Hafnium carbide		HfC	4160	7530
Iron carbide		Fe_3C	1840	3340

TABLE 69. MELTING POINTS OF PURE REFRACTORY MATERIALS (*Continued*)
Carbides (*Continued*)

Material	Mineral or common name	Formula	Melting point	
			°C	°F
Molybdenum carbide		Mo_2C	2380	4320
Silicon carbide		SiC	2700	4890
Tantalum carbide		TaC	3880	7020
Thorium carbide		ThC_2	2770	5020
Titanium carbide		TiC	3140	5670
Tungsten carbide		WC	2780	5036
Uranium carbide		UC	2400	4350
Vanadium carbide		VC	2830	5130
Zirconium carbide		ZrC	3530	6380
Zirconates				
Barium zirconate		$BaO \cdot ZrO_2$	2620	4748
Calcium zirconate		$CaO \cdot ZrO_2$	2350	4262
Magnesium zirconate		$MgO \cdot ZrO_2$	2150	3902
Strontium zirconate		$SrO \cdot ZrO_2$	>2800	>5072
Thorium zirconate		$ThO_2 \cdot ZrO_2$	2800	5072
Phosphates				
Aluminum phosphate		$AlPO_4$	>1500	>2732
Calcium phosphate		$Ca_3(PO_4)_2$	1670	3038
Calcium phosphate		$Ca_4 \cdot P_2O_9$	1630	2966
Calcium phosphate		$Ca_{10}P_6O_{13}$	1540	2804
Calcium phosphate-fluoride	Fluorapatite	$CaF_2 \cdot 3CaP_2O_8$	1630	2966
Calcium silicon phosphate		$5CaO \cdot SiO_2 \cdot P_2O_5$	1760	3200
Spinels				
Barium aluminate		$BaO \cdot Al_2O_3$	2000	3632
Beryllium aluminate	Chrysoberyl	$BeO \cdot Al_2O_3$	1870	3398
Calcium aluminate		$CaO \cdot Al_2O_3$	1600	2912
Cobalt aluminate		$CoO \cdot Al_2O_3$	1960	3560
Ferrous aluminate	Hercynite	$FeO \cdot Al_2O_3$	1600	2912
Ferrous chromite	Chromite	$FeO \cdot Cr_2O_3$	>1770	3218
Ferrous ferrite	Magnetite	$FeO \cdot F_2O_3$	1538*d*	2800
Magnesium aluminate	Spinel	$MgO \cdot Al_2O_3$	2135	3875
Magnesium chromite		$MgO \cdot Cr_2O_3$	>1780	3236
Magnesium ferrite	Magnesioferrite	$MgO \cdot Fe_2O_3$	>1780	3236
Nickel aluminate		$NiO \cdot Al_2O_3$	2020	3668
Strontium aluminate		$SrO \cdot Al_2O_3$	2020	3668
Zinc aluminate	Gahnite	$ZnO \cdot Al_2O_3$	1950	3542
Zinc ferrite		$ZnO \cdot Fe_2O_3$	1590	2894

In Table 70, the fusion points of a number of refractory bricks are given. These values were obtained with an optical pyrometer in a tube furnace under reducing conditions and, in many cases, will be slightly lower in value than a corresponding determination made in an oxidizing atmosphere.

TABLE 70. FUSION POINTS OF BRICKS MANUFACTURED FROM NATIVE CLAYS

Material	Fusion point	
Alumina, Fused	1750 to 2050	3182 to 3722
Bauxite	1732 to 1850	3150 to 3362
Carborundum (recrystallized)	2200 (decom.)	3992
Carbon	very high	
Chrome	1950 to 2200	3542 to 3992
Clay, native in:		
Arkansas	1615 to 1625	2939 to 2954
British Columbia	1615 to 1645	2939 to 2993
California	1657 to 1688	3015 to 3070
Colorado	1585 to 1796	2885 to 3265
England	1620 to 1657	2948 to 3015
Georgia	1685 to 1700	3065 to 3092
Idaho	1660 to 1700	3038 to 3092
Kentucky	1627 to 1718	2961 to 3124
Maryland	1595 to 1640	2903 to 2984
Missouri	1610 to 1750	2930 to 3182
Montana	1580	2876
New Jersey	1582 to 1677	2880 to 3051
New York	1685	3065
Ohio	1610 to 1782	2930 to 3240
Pennsylvania	1630 to 1757	2966 to 3195
Texas	1615	2939
Washington	1605 to 1638	2921 to 2980
Clays high in alumina	1802 to 1880	3276 to 3416
Graphite-clay	1605 to 1675	2921 to 3047
Kaolins (southern)	1645 to 1785	2993 to 3245
Magnesite	2200	3992
Mullite	1780 to 1800	3236 to 3272
Silica	1700	3090
Spinel	1693 to 2100	3079 to 3812
Zircon and Zirconia	2200 to 2700	3992 to 4892

5. Value of Fusion Points. The value of a fusion point in determining the possibility of a material for specific purposes has often been overestimated. What the fusion point does show is whether or not a material is unsuitable above a certain temperature. For example, if it should be desired to make a firebrick to be used with furnace temperatures of 1600°C (about 2910°F) and various samples of clays were selected, the fusion-point

test would eliminate at once all those with a fusion point equal to or below that temperature. However, a clay softening at 1850°C (about 3360°F) would not necessarily be better for this brick than another clay softening at 1750°C (about 3180°F).

The fusion point of a material is by no means a criterion of its ability to carry a load at high temperatures, which in actual use is of considerable importance in determining the maximum temperature at which it can be successfully used. For example, commercial magnesite has a fusion point of over 2000°C (about 3630°F); yet it will not carry a load at temperatures over 1400°C (about 2550°F) to 1500°C (about 2730°F). On the other hand, a mullite brick that has a fusion point of 1780°C (about 3230°F) will show no deformation at temperatures of 1727°C (about 3140°F).

6. Equilibrium Diagrams. The equilibrium diagrams in the refractory systems are particularly useful in studying problems in the manufacture and use of refractories. A thorough understanding of the equilibrium conditions will allow one to interpret the results of practical tests more accurately, although it should be remembered that ceramic reactions seldom reach complete equilibrium. In this chapter are included nearly all of the equilibrium diagrams that are now available dealing with the refractory systems.

Phase Rule. The construction and interpretation of the equilibrium diagram depend largely on the phase rule, which states

$$P + V = C + 2$$

where P = the number of phases
C = the number of components
V = the number of degrees of freedom

The following definitions applying to the equilibrium system are commonly used:

1. *System:* Any portion of the material universe that we choose to separate in thought from the rest of the universe for the purpose of considering and discussing the various changes that may occur within it under various conditions is called a "system."

2. *Phase:* The physically homogeneous but mechanically separable portions of the system are called its "phases."

3. *Components:* The number of components of a system at equilibrium is defined as the smallest number of independently variable constituents by means of which the composition of each phase can be quantitatively expressed.

4. *Variance of a System (Degree of Freedom):* In the application of the phase rule to the type of systems under consideration, the independently variable conditions usually taken into consideration are temperature, pressure, and concentration. The number of these variables, which must be arbitrarily fixed to define the system completely, is called the "variance" or "degree of freedom" of that system.

5. *Equilibrium:* An equilibrium exists in any system under a fixed set of conditions when the parts of the system do not undergo any change of properties with the passage

of time and provided the parts of the system have the same properties when the same conditions are again arrived at by a different procedure.

6. *Melting Point:* The temperature of transition of solid to liquid state at atmospheric pressure in which the liquid phase is of the same composition as the solid phase is known as the "congruent melting point" of the solid phase. This is in contradistinction to the transition of one solid phase into a second solid phase with the liberation of liquid of a different composition; the latter is called an "incongruent melting point."

7. *Transition Point:* When the pressure is the atmospheric pressure, the temperature at which two solid phases can coexist and at which the relative stability of the two forms undergoes change is known as the "transition point."

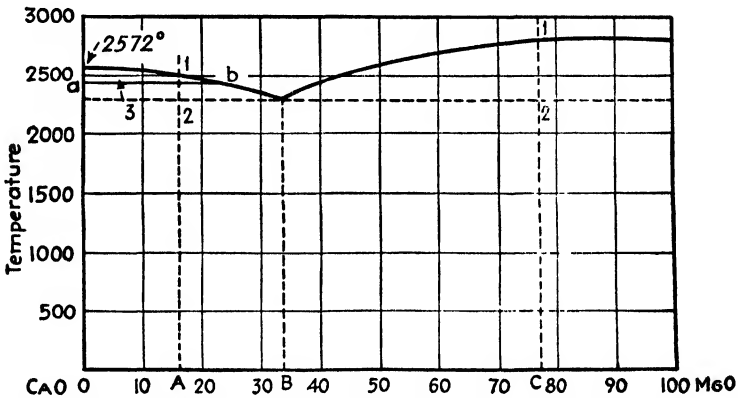


FIG. 182. Equilibrium diagram for lime and magnesia. (Weight per cent.)

Methods of Obtaining High-temperature Equilibrium Diagrams. Although the method of using cooling curves has been of great aid to the metallurgist, it has not been successful for high-temperature refractory materials because of the great undercooling encountered and the small heat evolved or absorbed compared with radiation exchange. Heating curves are somewhat more reliable but not generally useful for studies of refractories.

The method most used consists in heating the mixture at a given temperature until equilibrium is established and quenching suddenly to fix the structure developed. A microscopic examination will then show the crystalline phases present, if any.

Interpretation of the Equilibrium Diagram. For a full discussion of the interpretation of the equilibrium diagrams, reference should be made to Hall and Insley,[61] from whom the diagrams reproduced here have been taken. However, a very brief outline is given here to indicate the features of the simpler types of diagrams.

Let us first consider a phase diagram composed of two materials completely soluble in each other and forming no compound. As an example, we may take lime and magnesia, shown in the diagram in Fig. 182. It will

be noted that the solution of either material in the other lowers the freezing point and that at a composition of 33 per cent MgO, the lowest freezing point is reached. When a composition represented by *A* is considered, the melt is completely liquid above point 1; but at this point, CaO begins to crystallize out. At point 2, no liquid is left and the solid consists of mixed crystals of MgO and CaO. The same thing occurs at composition *C*, except that MgO first crystallizes out. At the composition *B*, CaO and MgO crystallize out simultaneously and there is no mixture of liquid and crystals as there are for all other compositions. This point is called the "eutectic point."

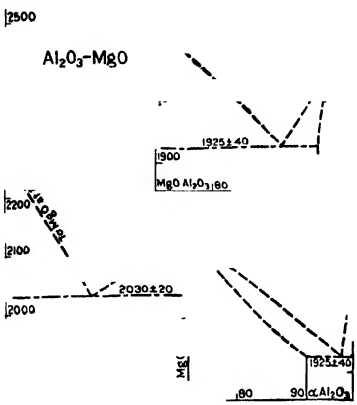


FIG. 183. Equilibrium diagram for magnesia and alumina. (*International Critical Tables.*)

Another example may be considered where two substances are completely soluble in each other but form a single compound, such as magnesia and alumina. The simplified equilibrium diagram for these materials is shown in Fig. 183. The compound spinel is formed of a composition containing 72 per cent MgO and 28 per cent Al_2O_3. The diagram may be divided into two portions, each one of which is similar to the preceding diagram.

It is possible to determine the relative amount of liquid and solid at any point of the diagram by the so-called "lever principle." Figure 182 gives the ratio of solid material at point 3 to liquid by

$$\frac{\text{Distance } b3}{\text{Distance } a3}$$

measuring along the horizontal line *ab*.

Equilibrium Diagrams for High-temperature Systems. In Table 71 are listed nearly all the diagrams of interest in the refractories field, together with the figure numbers of the corresponding diagrams that follow. These diagrams were taken from Hall and Insley, published in the *Journal of the American Ceramic Society.*[61]

TABLE 71. INDEX TO PHASE DIAGRAMS

Binary aluminates

$BaO \cdot Al_2O_3$ (Fig. 207)
$BeO \cdot Al_2O_3$ (Fig. 215)
$CaO \cdot Al_2O_3$ (Figs. 184, 206)
$CeO \cdot Al_2O_3$ (Figs. 199, 201)
$CoO \cdot Al_2O_3$ (Fig. 207)
$Cr_2O_3 \cdot Al_2O_3$ (Figs. 195, 200)
$Cu_2O \cdot Al_2O_3$ (Fig. 199)
$Fe_3O_4 \cdot Al_2O_3$ (Fig. 200)
$Ga_2O_3 \cdot Al_2O_3$ (Fig. 200)

TABLE 71. INDEX TO PHASE DIAGRAMS (*Continued*)

Binary aluminates (*Continued*)
$La_2O_3 \cdot Al_2O_3$ (Fig. 200)
$MgO \cdot Al_2O_3$ (Figs. 196, 207, 213)
$MnO_4 \cdot Al_2O_3$ (Fig. 200)
$NiO \cdot Al_2O_3$ (Fig. 207)
$SiO_2 \cdot Al_2O_3$ (Figs. 187, 199)
$SrO \cdot Al_2O_3$ (Fig. 207)
$ThO_2 \cdot Al_2O_3$ (Fig. 199)
$TiO_2 \cdot Al_2O_3$ (Figs. 197, 199)
$ZnO \cdot Al_2O_3$ (Fig. 198)
$ZrO_2 \cdot Al_2O_3$ (Figs. 199, 220)

Binary Chromites
$Al_2O_3 \cdot Cr_2O_3$ (Figs. 195, 200)
$CaO \cdot Cr_2O_3$ (Fig. 206)
$CeO_2 \cdot Cr_2O_3$ (Fig. 201)
$ZrO_2 \cdot Cr_2O_3$ (Fig. 220)

Binary Silicates
$Al_2O_3 \cdot SiO_2$ (Fig. 187, 199)
$BaO \cdot SiO_2$ (Fig. 188)
$CaO \cdot SiO_2$ (Fig. 189, 204)
$MgO \cdot SiO_2$ (Figs. 190, 213)
$SrO \cdot SiO_2$ (Fig. 191)
$TiO_2 \cdot SiO_2$ (Fig. 192)
$ZnO \cdot SiO_2$ (Fig. 193)
$ZrO_2 \cdot SiO_2$ (Fig. 194)

Binary Thorates
$BeO \cdot ThO_2$ (Fig. 216)
$CaO \cdot ThO_2$ (Fig. 204)
$MgO \cdot ThO_2$ (Fig. 225)
$ZrO_2 \cdot ThO_2$ (Fig. 217)

Binary Titanates
$CaO \cdot TiO_2$ (Fig. 204)
$MgO \cdot TiO_2$ (Fig. 210)
$ZrO_2 \cdot TiO_2$ (Fig. 220)

Binary Zirconates
$Al_2O_3 \cdot ZrO_2$ (Fig. 220)
$BaO \cdot ZrO_2$ (Fig. 218)
$BeO \cdot ZrO_2$ (Fig. 216)
$CaO \cdot ZrO_2$ (Figs. 203, 218)
$CeO_2 \cdot ZrO_2$ (Fig. 227)
$CoO \cdot ZrO_2$ (Fig. 219)
$Cr_2O_3 \cdot ZrO_2$ (Fig. 220)
$Fe_2O_3 \cdot ZrO_2$ (Fig. 220)
$La_2O_3 \cdot ZrO_2$ (Fig. 220)
$MgO \cdot ZrO_2$ (Figs. 213, 218)
$Mn_3O_4 \cdot ZrO_2$ (Fig. 220)
$NiO \cdot ZrO_2$ (Fig. 219)
$SrO \cdot ZrO_2$ (Fig. 218)
$ThO_2 \cdot ZrO_2$ (Fig. 217)
$TiO_2 \cdot ZrO_2$ (Fig. 220)
$ZnO \cdot ZrO_2$ (Fig. 219)

Binary Beryllia Systems
$Al_2O_3 \cdot BeO$ (Fig. 215)
$CaO \cdot BeO$ (Fig. 214)
$CeO_2 \cdot BeO$ (Fig. 216)
$CoO \cdot BeO$ (Fig. 214)
$Cr_2O_3 \cdot BeO$ (Fig. 215)
$Cu_2O \cdot BeO$ (Fig. 214)
$Fe_3O_4 \cdot BeO$ (Fig. 215)
$La_2O_3 \cdot BeO$ (Fig. 215)
$MgO \cdot BeO$ (Fig. 214)
$MnO_4 \cdot BeO$ (Fig. 215)
$NiO \cdot BeO$ (Fig. 214)
$ThO_2 \cdot BeO$ (Fig. 216)
$TiO_2 \cdot BeO$ (Fig. 216)
$ZrO_2 \cdot BeO$ (Fig. 216)

Binary Calcium Oxide Systems
$Al_2O_3 \cdot CaO$ (Figs. 184, 206)
$CeO_2 \cdot CaO$ (Fig. 204)
$CoO \cdot CaO$ (Fig. 205)
$Cr_2O_3 \cdot CaO$ (Fig. 206)
$Cu_2O \cdot CaO$ (Fig. 205)
$Fe_2O_3 \cdot CaO$ (Fig. 206)
$MgO \cdot CaO$ (Figs. 202, 205, 208)
$MnO_2 \cdot CaO$ (Fig. 206)
$NiO \cdot CaO$ (Fig. 205)
$SiO_2 \cdot CaO$ (Fig. 189, 204)
$ThO_2 \cdot CaO$ (Fig. 204)
$TiO_2 \cdot CaO$ (Fig. 204)
$ZrO_2 \cdot CaO$ (Figs. 203, 204)

Ceria Systems
$Al_2O_3 \cdot CeO_2$ (Fig. 201)
$BeO \cdot CeO_2$ (Fig. 216)
$Cr_2O_3 \cdot CeO_2$ (Fig. 201)
$Fe_3O_4 \cdot CeO_2$ (Fig. 201)
$MgO \cdot CeO_2$ (Fig. 213)
$Mn_3O_4 \cdot CeO_2$ (Fig. 201)
$ZrO_2 \cdot CeO_2$ (Fig. 227)

Binary Magnesia Systems
$Al_2O_3 \cdot MgO$ (Figs. 196, 207, 213)
$BaO \cdot MgO$ (Fig. 212)
$BeO \cdot MgO$ (Fig. 212)
$CaO \cdot MgO$ (Figs. 202, 205)
$CeO_2 \cdot MgO$ (Fig. 213)
$CoO \cdot MgO$ (Fig. 208)
$Cu_2O \cdot MgO$ (Fig. 212)
$Fe_3O_4 \cdot MgO$ (Fig. 213)
$Mn_3O_4 \cdot MgO$ (Fig. 213)

TABLE 71. INDEX TO PHASE DIAGRAMS (*Continued*)

Binary Magnesia Systems (*Continued*)
NiO·MgO (Fig. 209)
SiO_2·MgO (Fig. 213)
SrO·MgO (Fig. 212)
ThO_2·MgO (Fig. 225)
TiO_2·MgO (Fig. 210)
ZrO_2·MgO (Figs. 211, 213, 218)
Ternary Aluminates
BeO·MgO·Al_2O_3 (Fig. 231)
BeO·ThO_2·Al_2O_3 (Fig. 230)
BeO·ZrO_2·Al_2O_3 (Fig. 229)
CaO·MgO·Al_2O_3 (Fig. 232)
CaO·SiO_2·Al_2O_3 (Fig. 224)
MgO·Cr_2O_3·Al_2O_3 (Fig. 233)
MgO·SiO_2·Al_2O_3 (Fig. 223)
ZnO·SiO_2·Al_2O_3 (Fig. 222)
Ternary Silicates
CaO·Al_2O_3·SiO_2 (Fig. 224)
CaO·MgO·SiO_2 (Fig. 221)
MgO·Al_2O_3·SiO_2 (Fig. 223)
ZnO·Al_2O_3·SiO_2 (Fig. 222)
Ternary Zirconates
BeO·Al_2O_3·ZrO_2 (Fig. 229)
BeO·CaO·ZrO_2 (Fig. 228)
BeO·CeO_2·ZrO_2 (Fig. 227)
CaO·ThO_2·ZrO_2 (Fig. 226)
MgO·ThO_2·ZrO_2 (Fig. 225)

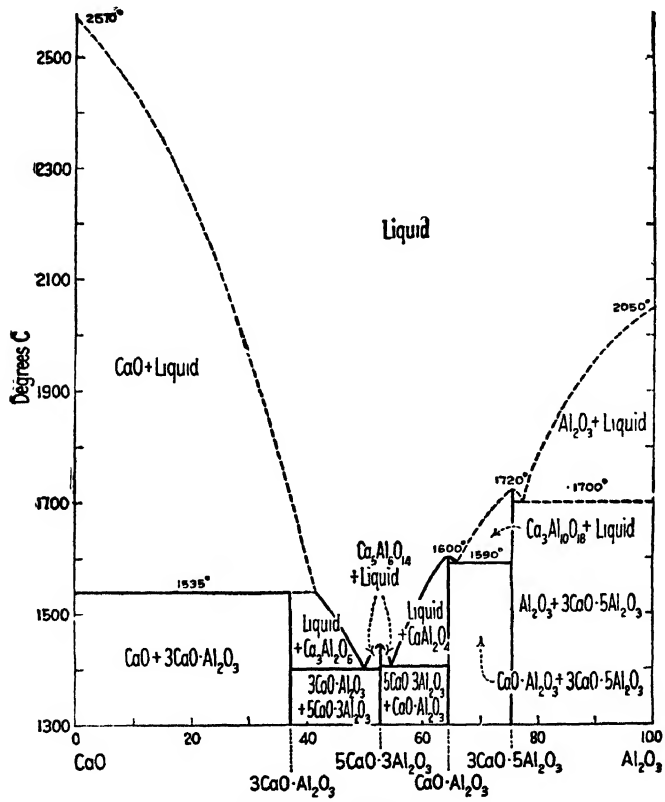


FIG. 184. Mol per cent.

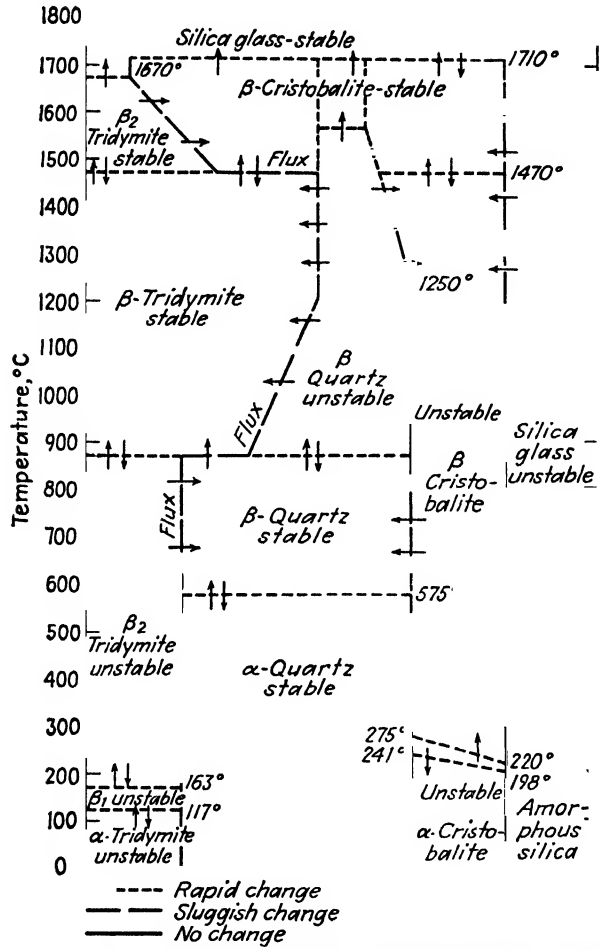


FIG. 185. Stability relations of the silica minerals. (*Modified from J. S. McDowell, Trans. Am. Inst. Mining Met. Engrs.*, **57**, 7, 1917.)

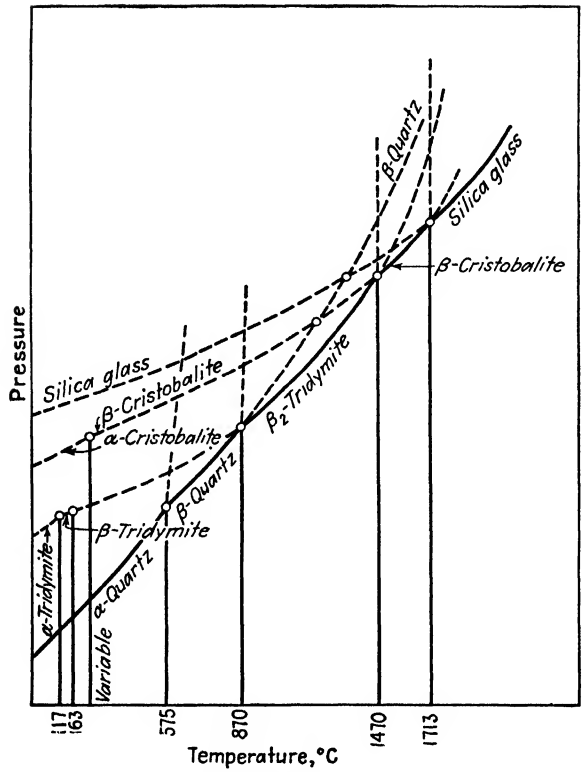


FIG. 186. Vapor pressure (stability) relations of the silica minerals. (*C. N. Fenner, Am. J. Sci., 4th Ser.*, **36**, 338, 1913; *silica glass–β-cristobalite inversion point from J. W. Greig, ibid., 5th Ser.*, **13**, 1–44, 1927.)

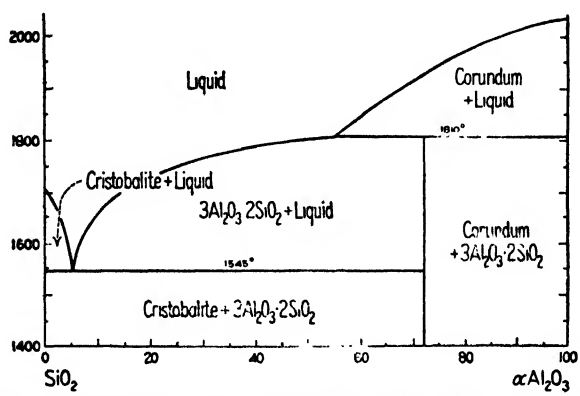


FIG. 187. System α-Al_2O_3–SiO_2. (*N. L. Bowen and J. W. Greig, J. Am. Ceram. Soc.*, **7**, 4, 242, 1924.)

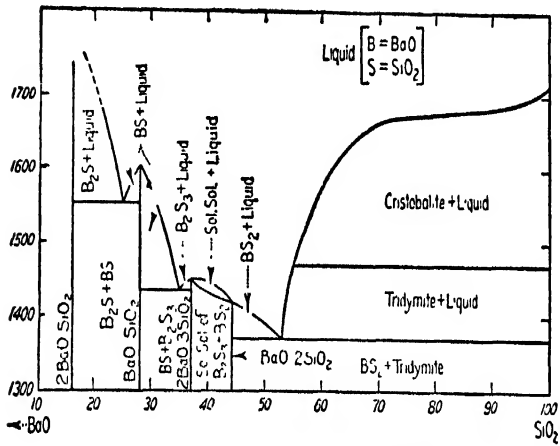


FIG. 188. System BaO–SiO_2. (*P. Eskola, Am. J. Sci., 5th Ser.*, **4**, 345, 122; *modified by J. W. Greig, Am. J. Sci., 5th Ser.*, **13**, 27, 1927.)

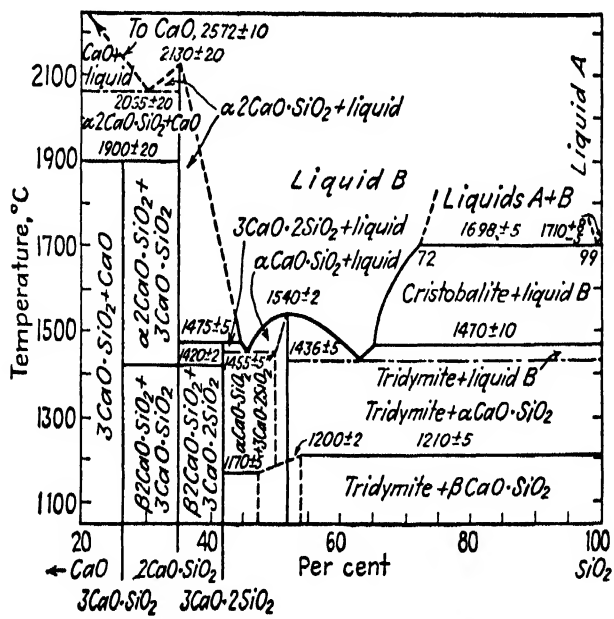


FIG. 189. System CaO–SiO_2. (*G. A. Rankin and F. E. Wright, Am. J. Sci., 4th Ser.*, **39**, 5, 1915; *modified by J. W. Greig, ibid., 5th Ser.*, **13**, 1–44, 1927.)

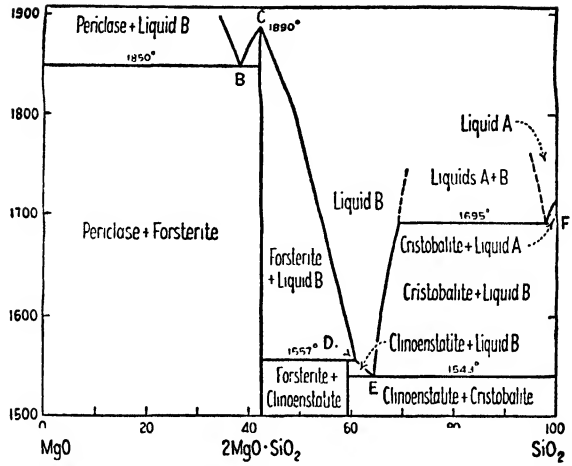


FIG. 190. System MgO–SiO_2. (*N. L. Bowen and Olaf Anderson, Am. J. Sci., 4th Ser.*, **37**, 488, 1914; *modified by J. W. Greig, ibid., 5th Ser.*, **13**, *pp.* 15, 133–54, 1927.)

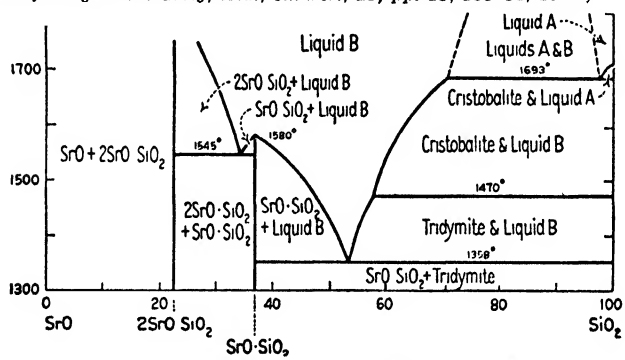


FIG. 191. System SrO–SiO_2. (*P. Eskola, Am. J. Sci., 5th Ser.*, **4**, 336, 1922; *modified by J. W. Greig, ibid., 5th Ser.*, **13**, 19, 1927; *see also F. C. Kracek, J. Am. Chem. Soc.*, **52** (4) 1440, 1930.)

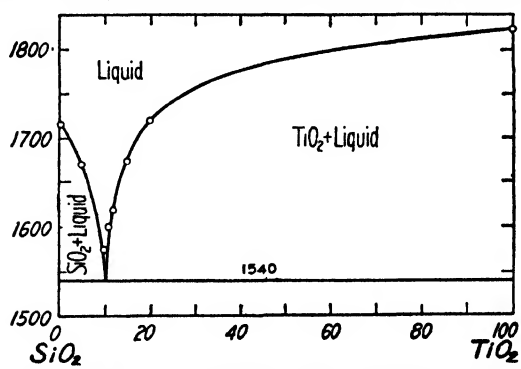


FIG. 192. System SiO_2–TiO_2. (*E. N. Bunting, Bur. Standards J. Research*, **11**, 723, 1933; *R. P.* **619.**)

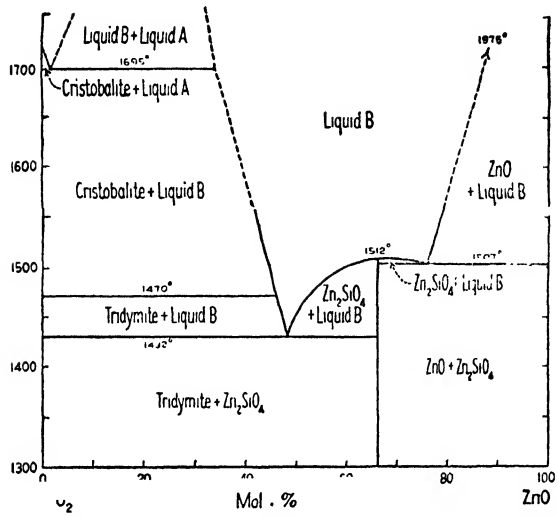


FIG. 193. System ZnO–SiO_2. (*E. N. Bunting, Bur. Standards J. Research*, **4**, 134, 1930; *R. P.* 136; *see also E. N. Bunting, J. Am. Ceram. Soc.*, **13** (1) 8, 1930.)

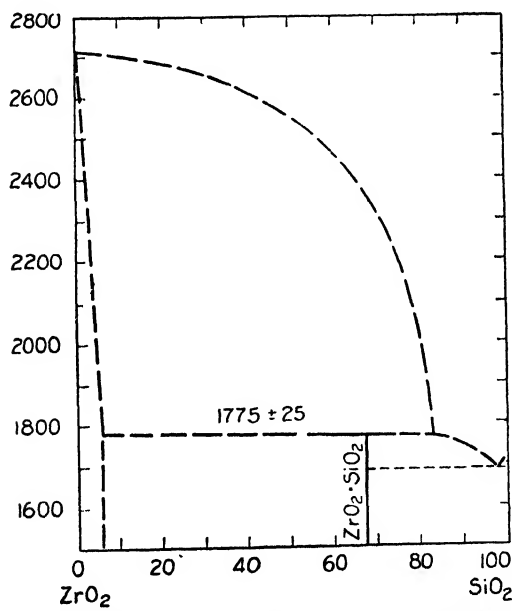


FIG. 194. System SiO_2–ZrO_2. (*R. F. Geller and P. J. Yavorsky, J. Research Nat. Bur. Standards*, **35** (1) 109, 1945; *R. P.* 1662.)

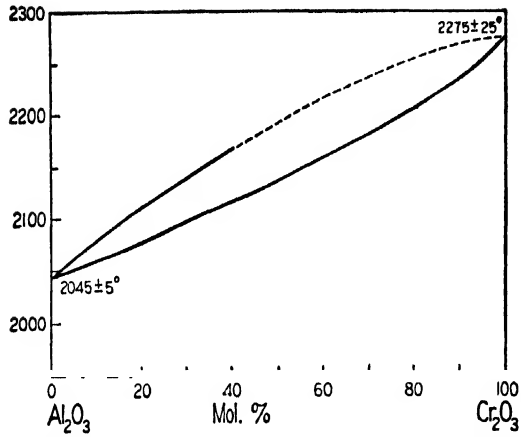


FIG. 195. System α-Al_2O_3–Cr_2O_3. (*E. N. Bunting, Bur. Standards J. Research*, **6** (6) 948, 1931; *R. P.* 317.)

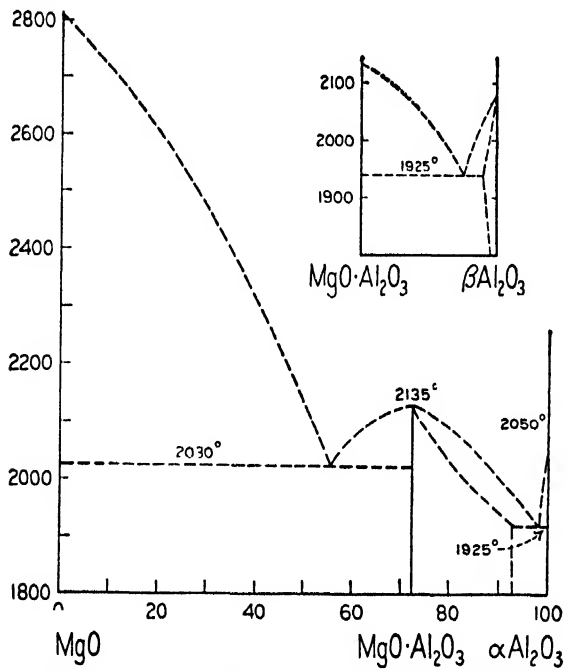


FIG. 196. Systems MgO–α-Al_2O_3 and MgO–β-Al_2O_3. (*G. A. Rankin and H. E. Merwin, J. Am. Chem. Soc.*, **38**, 571, 1916.)

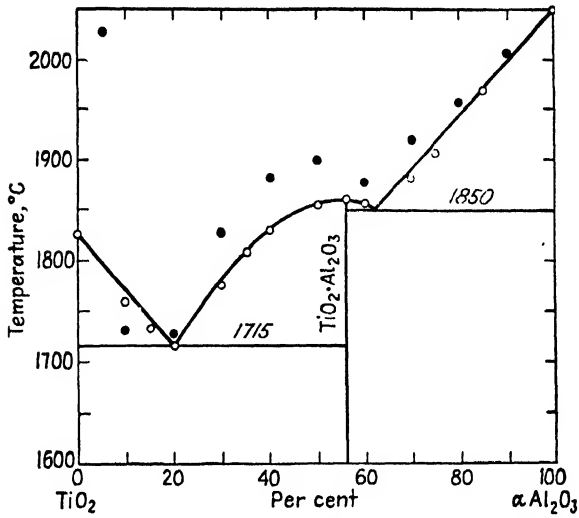


FIG. 197. System α-Al_2O_3–TiO_2. (*E. N. Bunting, Bur. Standards J. Research*, **11**, 725, 1933; *solid dots by H. v. Wartenberg and H. J. Reusch, Z anorg. u. allgem. Chem.*, **207**, 10, 1932.)

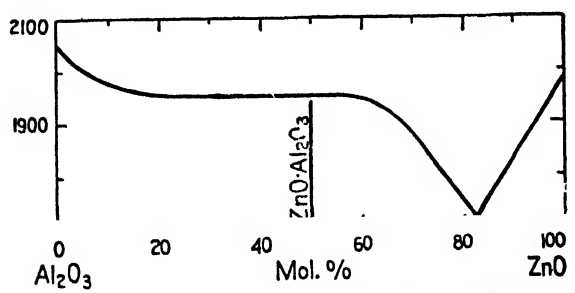


FIG. 198. Liquidus curve and system ZnO–Al_2O_3. (*E. N. Bunting, Bur. Standards J. Research*, **8** (2) 280, 1932; *R. P.* 413.)

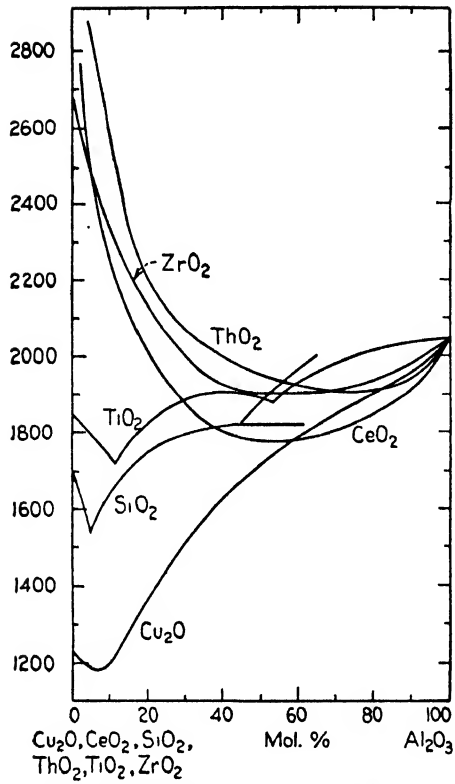


FIG. 199. Liquidus curves of systems Cu_2O–Al_2O_3, Al_2O_3–CeO_2, Al_2O_3–SiO_2, Al_2O_3–ThO_2, Al_2O_3–TiO_2, and Al_2O_3–ZrO_2. (*H. von Wartenberg and H. J. Reusch, Z. anorg. u. allgem. Chem.*, **207**, 18, 1932.)

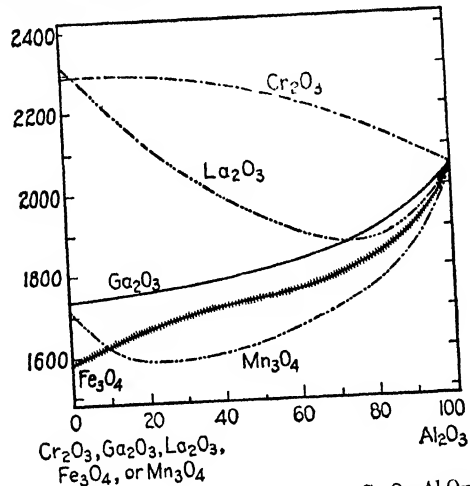


FIG. 200. Liquidus curves of systems Al_2O_3–Cr_2O_3, Al_2O_3–Ga_2O_3, Al_2O_3–La_2O_3, Al_2O_3–Fe_3O_4, and Al_2O_3–Mn_3O_4. (*H. von Wartenberg and H. J. Reusch, Z. anorg. u. allgem. Chem.*, **207**, 19, 1932.)

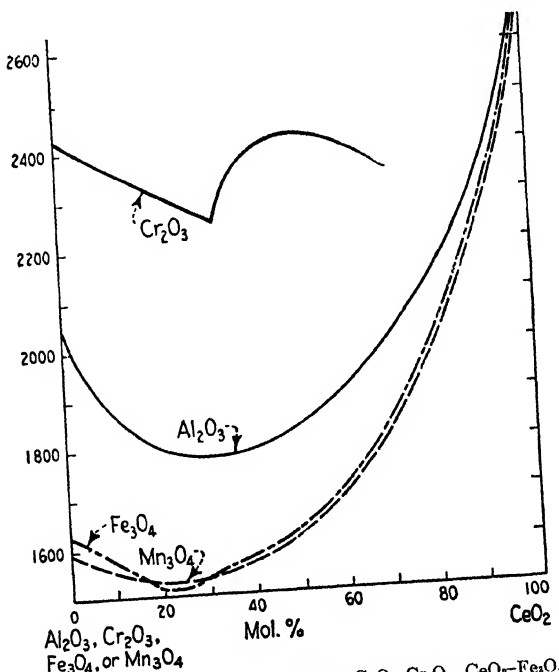


FIG. 201. Liquidus curves of systems CeO_2–Al_2O_3, CeO_2–Cr_2O_3, CeO_2–Fe_3O_4, CeO_2–Mn_3O_4. (*H. von Wartenberg and K. Eckhardt, Part VIII, Z. anorg. u. allgem. Chem.*, **232**, 184, 1937.)

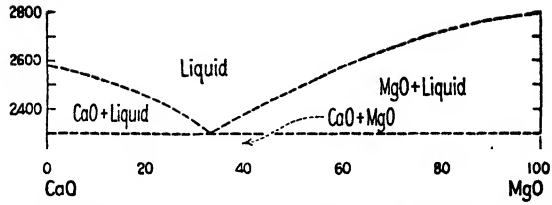


FIG. 202. System CaO–MgO. (*G. A. Rankin and H. E. Merwin, J. Am. Chem. Soc.*, **38**, 571, 1916.)

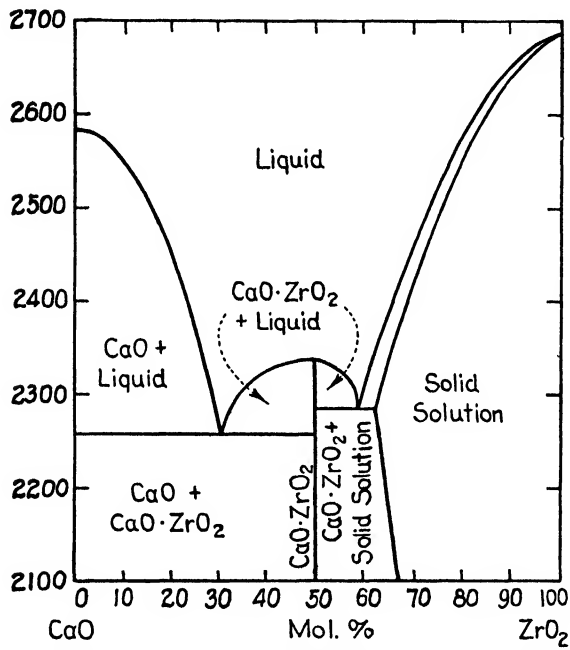


FIG. 203. System CaO–ZrO_2. (*O. Ruff, F. Ebert, and E. Stephan, Z. anorg. u. allgem. Chem.*, **180**, 219, 1929.)

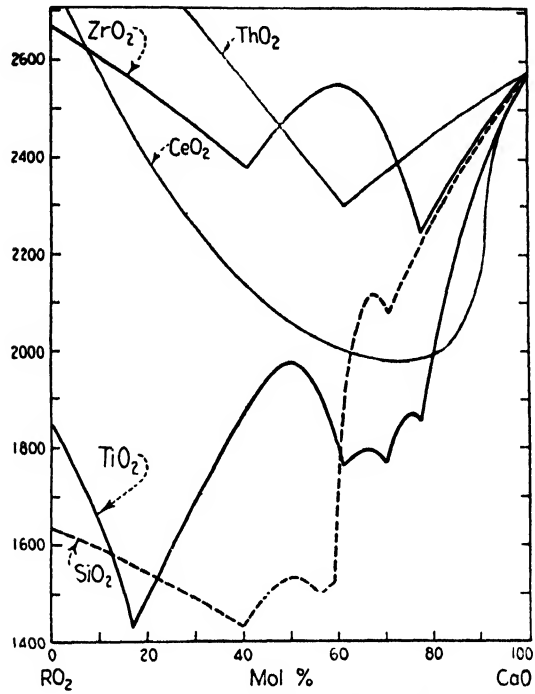


FIG. 204. Liquidus curves of systems CaO–CeO_2, CaO–SiO_2, CaO–ThO_2, CaO–TiO_2, and CaO–ZrO_2. (*H. v. Wartenberg, Z. anorg. u. allgem. Chem.*, **230**, 267, 1937.)

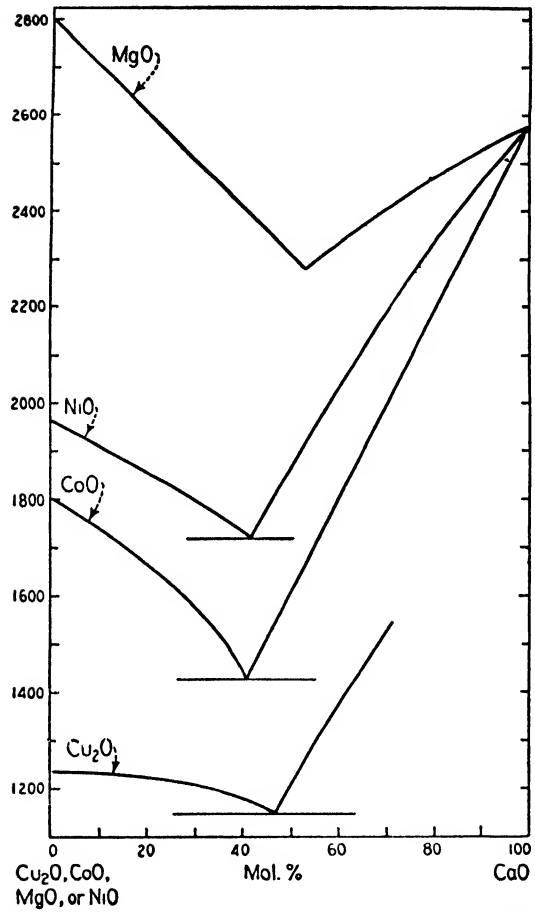


FIG. 205. Liquidus curves of systems Cu_2O–CaO, CaO–CoO, CaO–MgO, and CaO–NiO. (*H. v. Wartenberg, H. J. Reusch, and E. Saran, Part VII, Z. anorg. u. allgem. Chem.*, **230**, 265, 1937.)

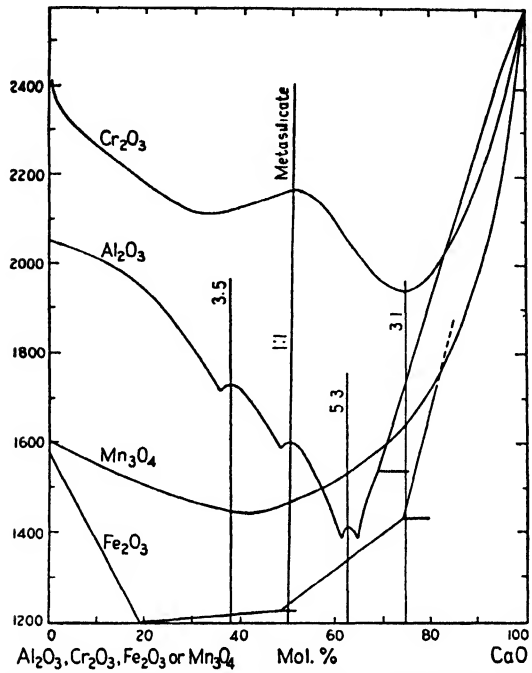


FIG. 206. Liquidus curves of systems $CaO-Al_2O_3$, $CaO-Cr_2O_3$, $CaO-Fe_2O_3$, and $CaO-Mn_3O_4$. *H. v. Wartenberg, H. J. Reusch, and E. Saran, Part VII, Z. anorg. u. allgem. Chem.*, **230**, 266, 1937.)

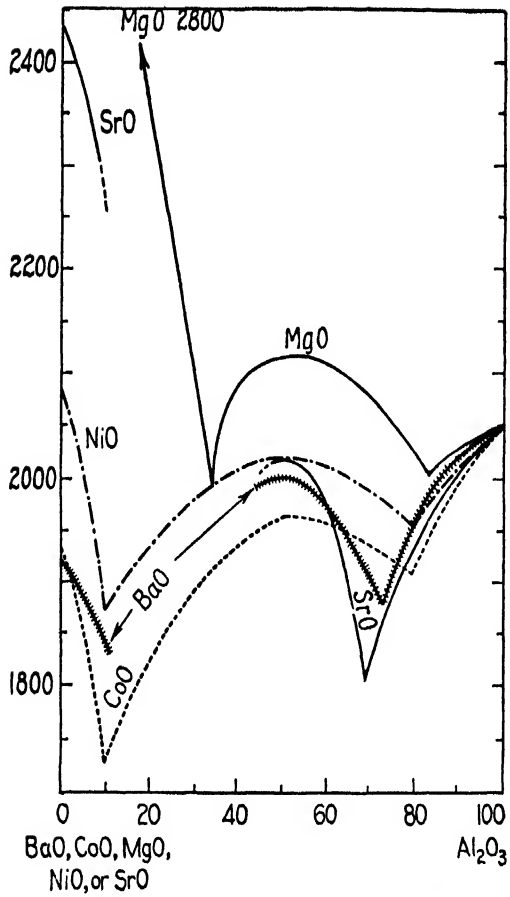


FIG. 207. Liquidus curves of systems $BaO-Al_2O_3$, $CoO-Al_2O_3$, $MgO-Al_2O_3$, $NiO-Al_2O_3$, and $SrO-Al_2O_3$. (*H. von Wartenberg and H. J. Reusch, Z. anorg. u. allgem. Chem.*, **207**, 18, 1932.)

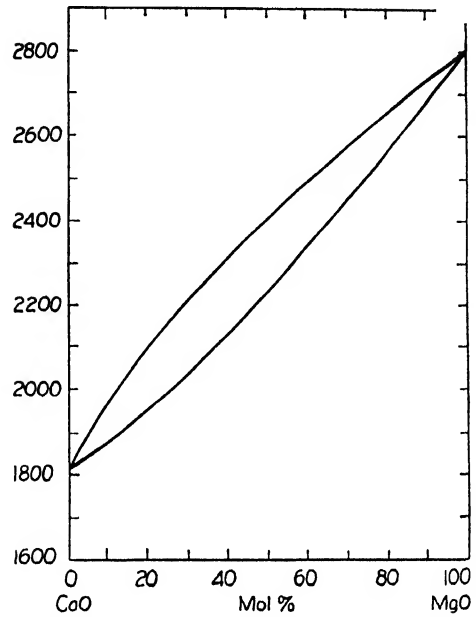


FIG. 208. System CoO–MgO. (*H. v. Wartenberg and E. Prophet, Z. anorg. u. allgem. Chem.*, **208**, 379, 1932.)

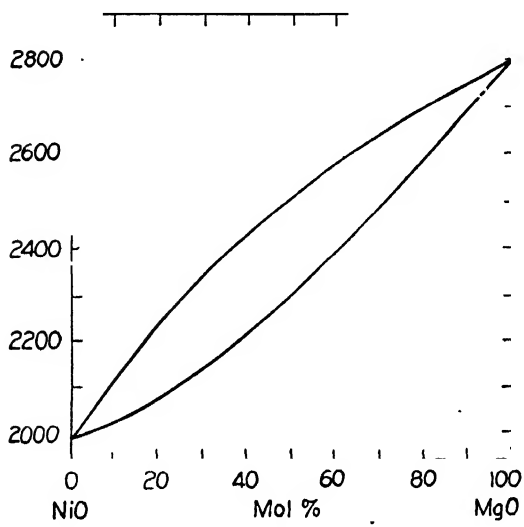


FIG. 209. System MgO–NiO. (*H. v. Wartenberg and E. Prophet, Z. anorg. u. allgem. Chem.*, **208**, 379, 1932.)

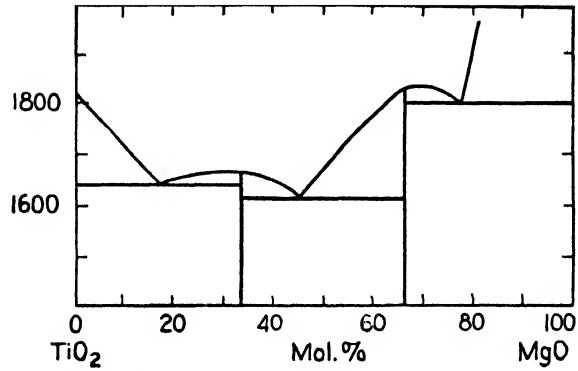


FIG. 210. System MgO–TiO_2. (*H. v. Wartenberg and E. Prophet, Z. anorg. u. allgem. Chem.*, **208**, 373, 1932.)

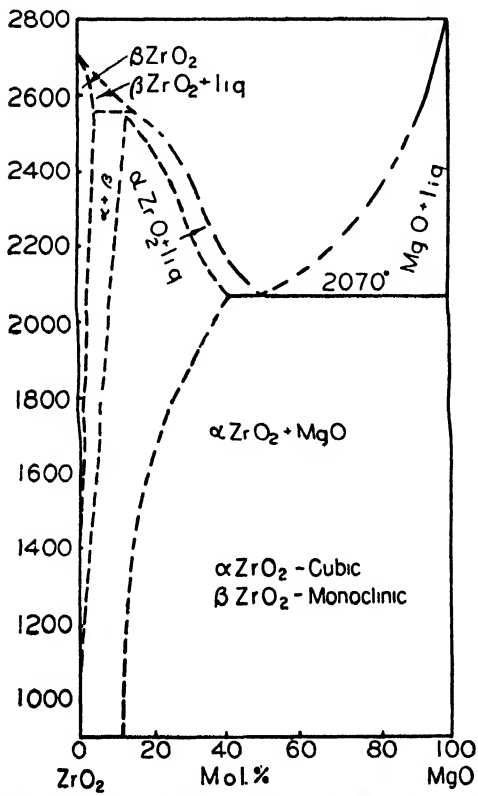


FIG. 211. System MgO–ZrO_2. (*N. A. Zhirnova, J. Applied Chem.* (*U.S.S.R.*), **12**, 1279, 1939.)

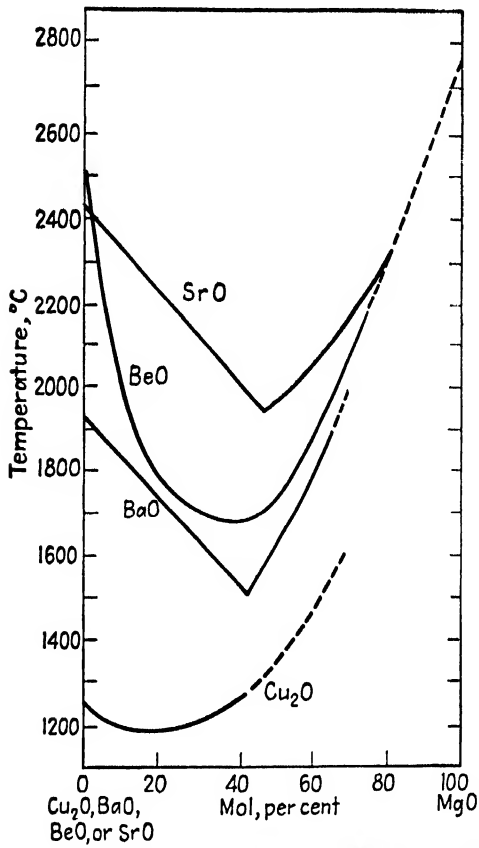


FIG. 212. Liquidus curves of systems Cu_2O–MgO, BaO–MgO, BeO–MgO, and MgO–SrO. *Note:* The MgO–BeO curve has been corrected as shown in FIG. 214. (*H. von Wartenberg and E. Prophet, Part V, Z. anorg. u. allgem. Chem.*, **208**, 378, 1932.)

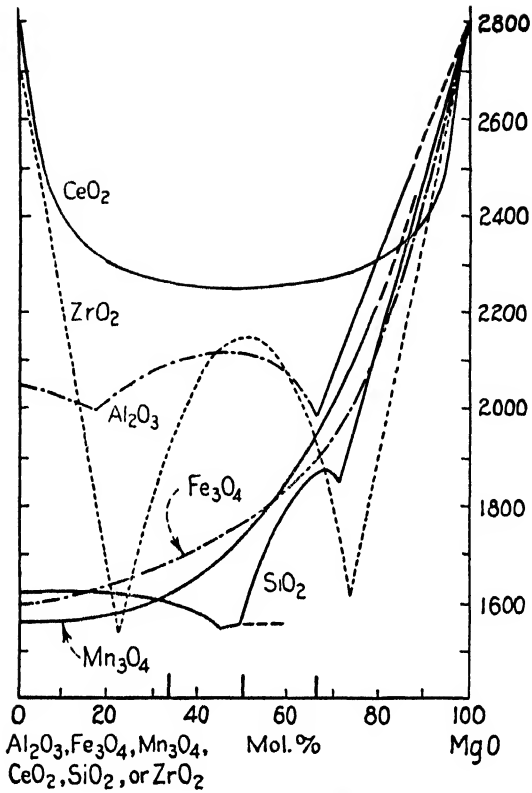


FIG. 213. Liquidus curves of systems MgO–Al_2O_3, MgO–Fe_3O_4, MgO–Mn_3O_4, MgO–CeO_2, MgO–SiO_2, and MgO–ZrO_2. (*H. von Wartenberg and E. Prophet, Z. anorg. u. allgem. Chem.*, **208**, 379, 1932; *the* CeO_2, *curve from Wartenberg and K. Eckhardt, Part VIII, ibid.*, **232**, 184, 1937.)

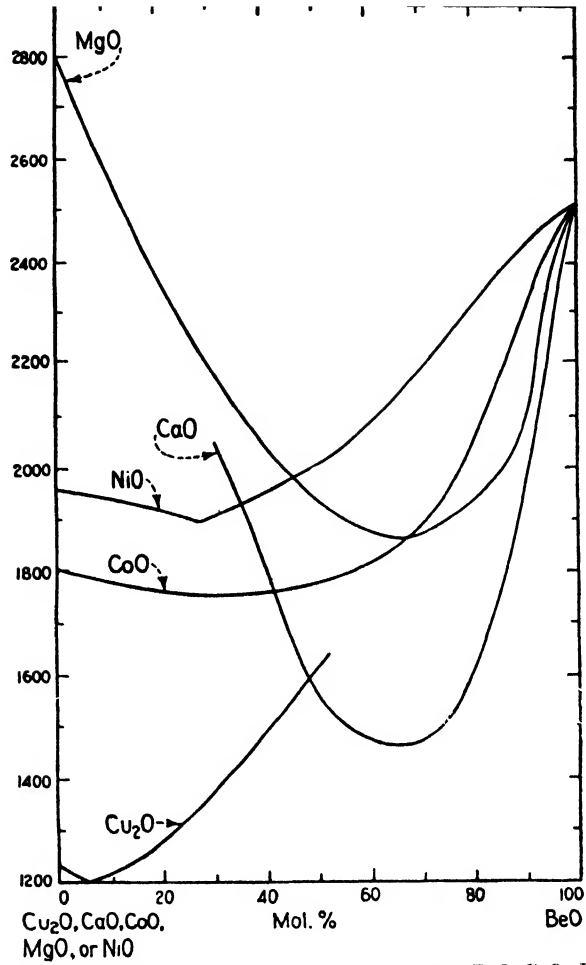


FIG. 214. Liquidus curves of systems BeO–Cu_2O, BeO–CaO, BeO–CoO, BeO–MgO, and BeO–NiO. (*H. v. Wartenberg, H. J. Reusch, and E. Saran, Part VII, Z. anorg. u. allgem. Chem.*, **230**, 275, 1937.)

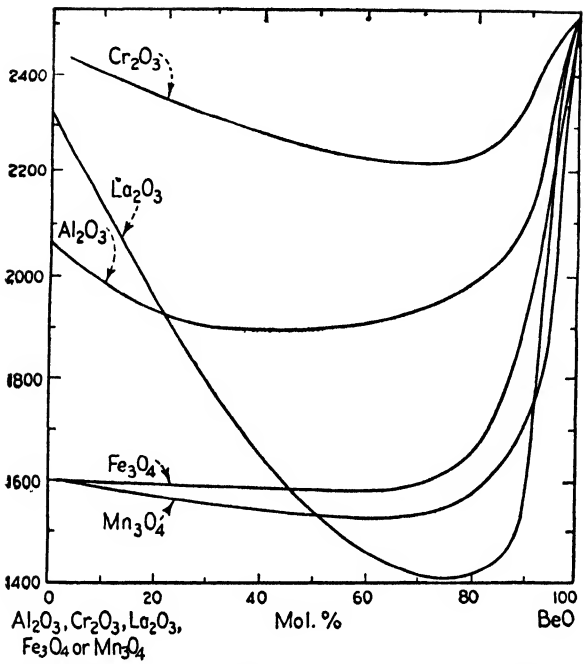


FIG. 215. Liquidus curves of systems BeO–Al_2O_3, BeO–Cr_2O_3, BeO–La_2O_3, BeO–Fe_3O_4, and BeO–Mn_3O_4. (*M. Dukelski, Z. anorg. Chem.*, **50**, 47, 1906.)

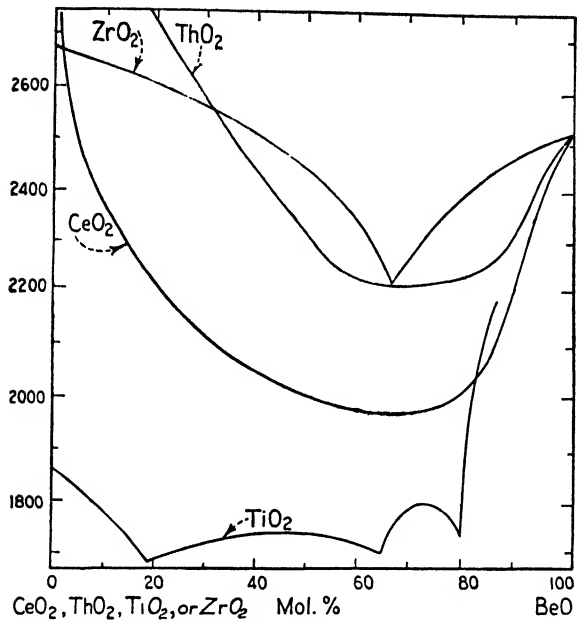


FIG. 216. Liquidus curves of systems BeO–CeO_2, BeO–ThO_2, BeO–TiO_2, and BeO–ZrO_2. (*M. Dukelski, Z. anorg. Chem.*, **50**, 47, 1906.)

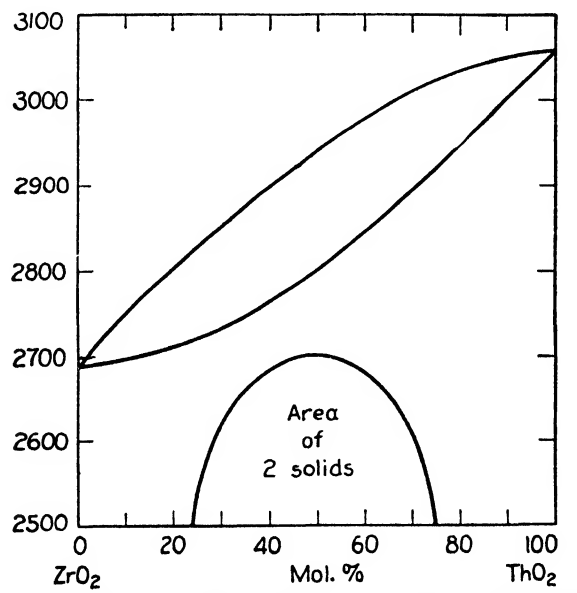


FIG. 217. System ThO_2–ZrO_2; probable diagram. (*O. Ruff, F. Ebert, and H. Woitinek, Z. anorg. u. allgem. Chem.*, **180**, 255, 1929.)

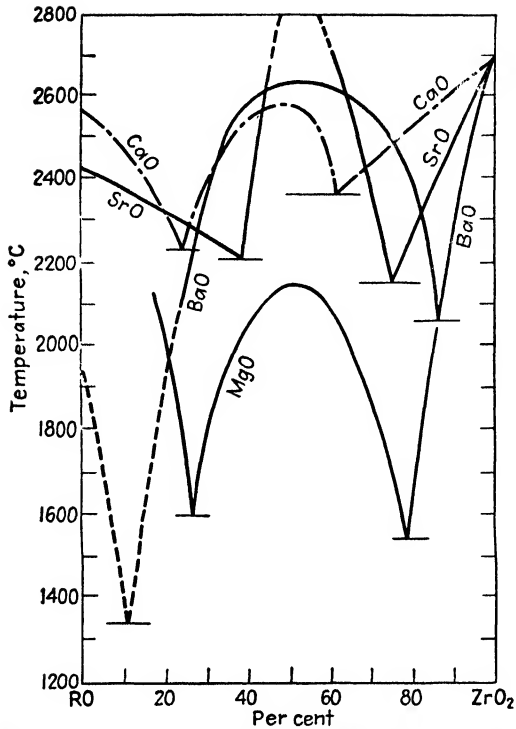


FIG. 218. Melting curves of $BaO-ZrO_2$, $CaO-ZrO_2$, $MgO-ZrO_2$, and $SrO-ZrO_2$. (*H. von Wartenberg and W. Gurr, Z. anorg. u. allgem. Chem.*, **196**, 381, 1931.)

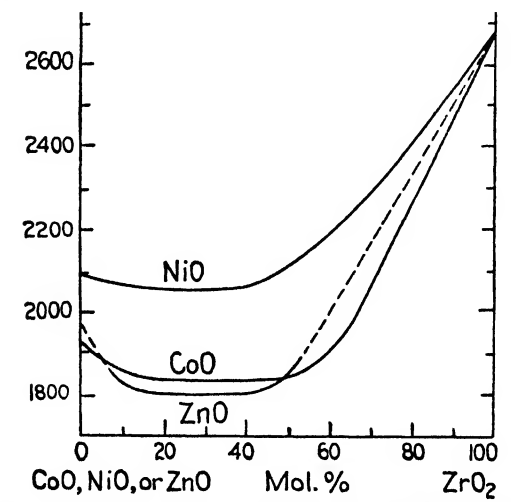


FIG. 219. Liquidus curves of systems $CoO-ZrO_2$, $NiO-ZrO_2$, and $ZnO-ZrO_2$. (*H. von Wartenberg and W. Gurr, Z. anorg. u. allgem. Chem.*, **196**, 381, 1931.)

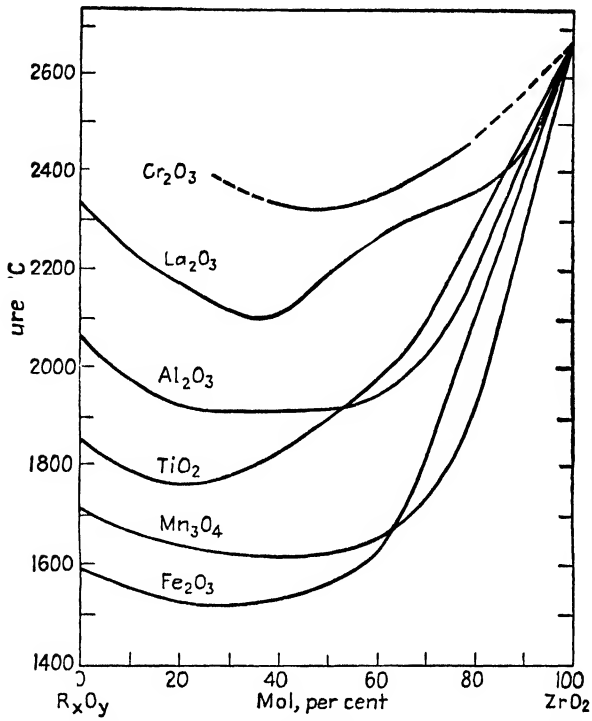


FIG. 220. Liquidus curves of systems Al_2O_3–ZrO_2, Cr_2O_3–ZrO_2, Fe_2O_3–ZrO_2, La_2O_3–ZrO_2, Mn_3O_4–ZrO_2, and TiO_2–ZrO_2. (*H. von Wartenberg and W. Gurr, Z. anorg. u. allgem. Chem.*, **196**, 381, 1931; *the* La_2O_3 *curve from Wartenberg and K. Eckhardt, Part VIII, ibid.*, **232**, 186, 1937.)

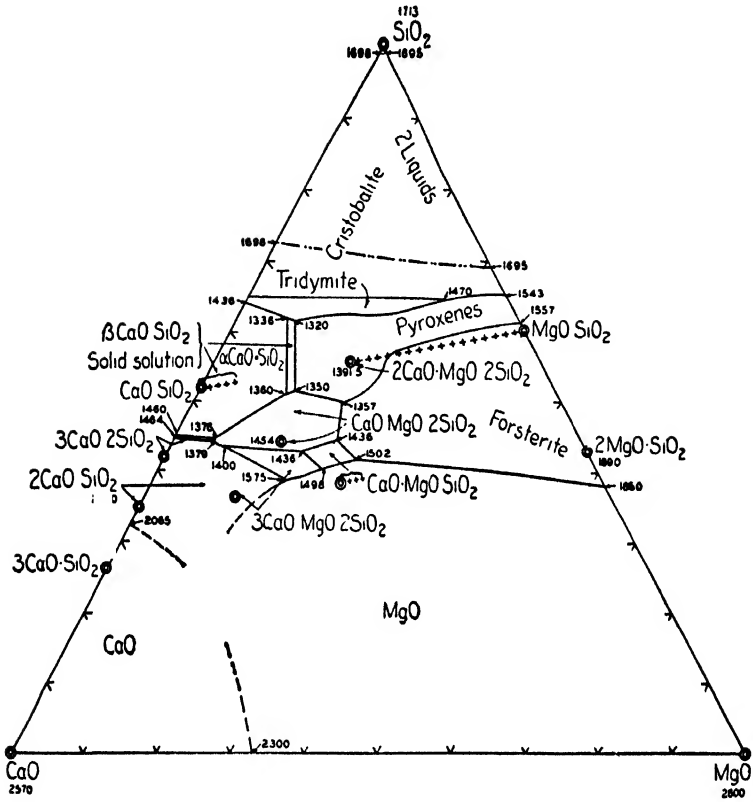


FIG. 221. System CaO–MgO–SiO_2. (*E. F. Osborn, J. Am. Ceram. Soc.*, **26** (10) 322, 1943.)

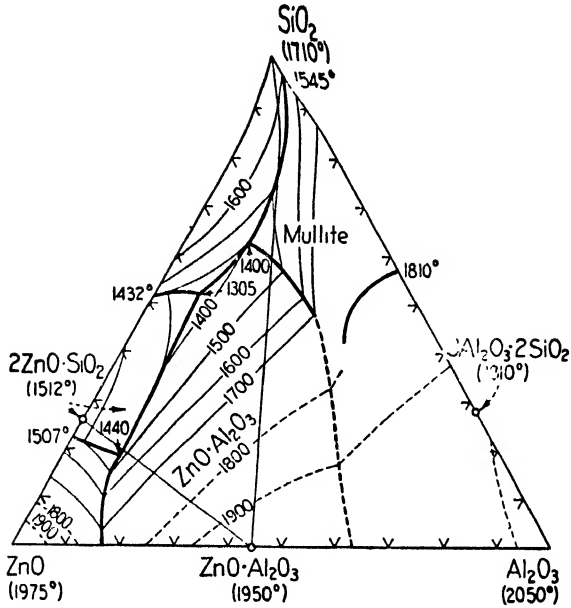


FIG. 222. System $ZnO-Al_2O_3-SiO_2$. (*E. N. Bunting, Bur. Standards J. Research*, **8** (2) 286, 1932; *R. P.* 413.)

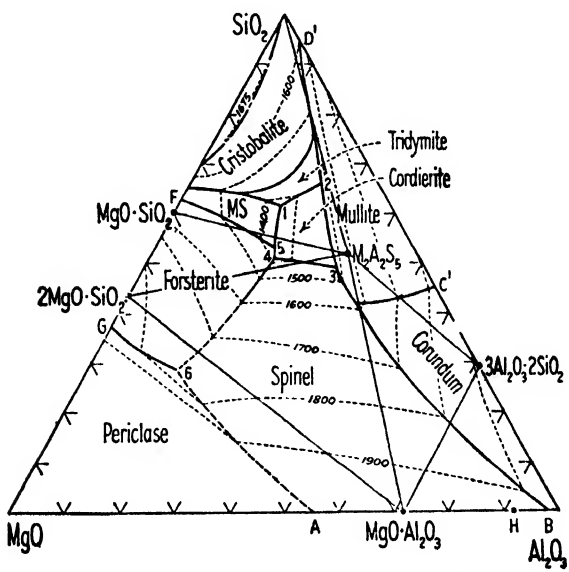


FIG. 223. System $MgO-Al_2O_3-SiO_2$. (*G. A. Rankin and H. E. Merwin, Am. J. Sci., 4th Ser.*, **45**, 322, 1918; *modified according to J. W. Greig, ibid., 5th Ser.*, **13**, 1–44, 1927.)

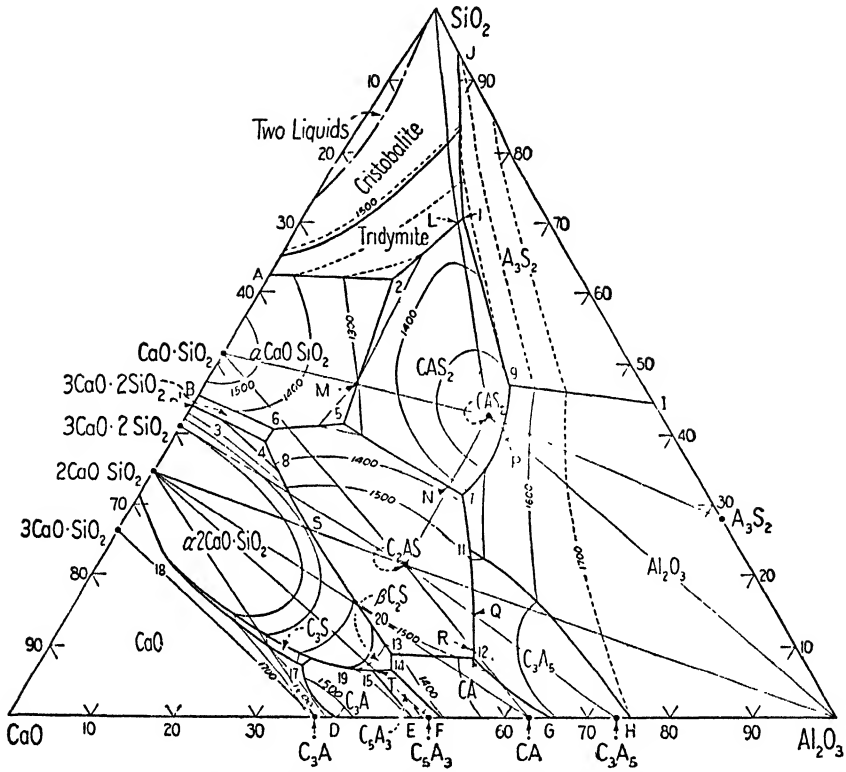


FIG. 224. System CaO–Al_2O_3–SiO_2; C = CaO, A = Al_2O_3, and S = SiO_2. (*J. W. Greig, Am. J. Sci., 5th Ser.*, **13**, 41, 1927; *G. A. Rankin and F. E. Wright, Am. J. Sci., 4th Ser.*, **39**, 52, 1915.)

Pt	Crystal phases	CaO	Al_2O_3	SiO_2	Temp
A	S, CS	37.0		63.0	1436
B	CS, CS_2	54.5		45.4	1455
B′	CS_2, C_2S	55.5		44.5	1475
C	C_2S, C	67.5		32	2065
D	C, C_3A	59.0	41.0		1535
E	C_3A, C_5A_3	50 0	50.0		1395
F	C_5A_3, CA	47.0	53.0		1400
G	CA, CA_5	33.5	66.5		1590
H	CA_5, A	24.0	76.0		1700
I	A, A_3S_2		55.0	45.0	1800
J	A_3S_2, S		5.5	94.5	1545
L	CAS_2, S	10.5	19.5	70.0	1359
M	CAS_2, CS	34.1	18.6	47.7	1299
N	CAS_2, C_2AS	30.2	36.8	33.0	1385
O	C_2AS, CS	45.7	13.2	41.1	1316
P	CAS_2, A	19.3	39.3	41.4	1547
Q	C_2AS, C_3A_5	35.0	50.8	14.2	1552
R	C_2AS, CA	37.8	52.9	9.3	1512
S	C_2AS, C_2S	49.6	23.7	26.7	1545
T	C_2S, C_5A_3	51.3	41.8	6.9	1350
	CaO	100.0			2570
	Al_2O_3		100.0		2050
	SiO_2			100.0	1713
	$3CaO·5Al_2O_3$	24.8	75.2		1720
	$CaO·Al_2O_3$	35.4	64.6		1600
	$5CaO·3Al_2O_3$	47.8	52.5		1455

Pt	Crystal phases	CaO	Al_2O_3	SiO_2	Temp
1	CAS_2, A_3S_2, S	9.8	19.8	70.4	1345
2	CAS_2, S, α-CS	23.3	14.7	62.2	1170
3	CS_2, C_2S, β-C_2S	53.0	4 2	42.8	1415
4	β-C_2S, C_2S, C_2AS	48.2	11.9	39.2	1335
5	CAS_2, C_2AS, α-CS	38 0	20.0	42.0	1265
6	C_2AS, CS_2, α-CS	47 2	11.8	41 0	1310
7	CAS_2, C_2AS, A	29 2	39.0	31.8	1380
8	α-C_2S, β-C_2S, C_2AS	49 0	14.4	36.6	1415
9	CAS_2, A, A_3S_2	15 6	36 5	47.9	1512
11	C_2A_5, C_2AS, A	31.2	44.5	24.3	1475
12	C_2AS, CA, C_3A_5	37.5	53.2	9.3	1505
13	C_2AS, β-C_2S, CA	48.3	42.0	9.7	1512
14	β-C_2S, CA, C_5A_3	49.5	43.7	6.8	1335
15	β-C_2S, C_3A, C_5A_3	52.0	41.2	6.8	1335
16	C_2S, α-C_2S, C_3A	58.3	33.0	8.7	1455
17	C, C_3S, C_3A	59 7	32.8	7.5	1470
18	C, α-C_2S, C_3S	68.4	9.2	22.4	1900
	$3CaO·Al_2O_3$	62.2	37.8	....	1535
	$CaO·SiO_2$	48.2	....	51.8	1540
	$3CaO·2SiO_2$	58.2	.....	41.8	1475
	α-$2CaO·SiO_2$	65.0	.....	35.0	2130
	$3CaO·SiO_2$	73.6	.....	26.4	1900
	$3Al_2O_3·2SiO_2$	....	71.8	28.2	1810
	$CaO·Al_2O_3$, $2SiO_2$	20.1	36.6	43.3	1550
	$2CaO·Al_2O_3·SiO_2$	40.8	37.2	22.0	1590

C = CaO; A = Al_2O_3; S = SiO_2.

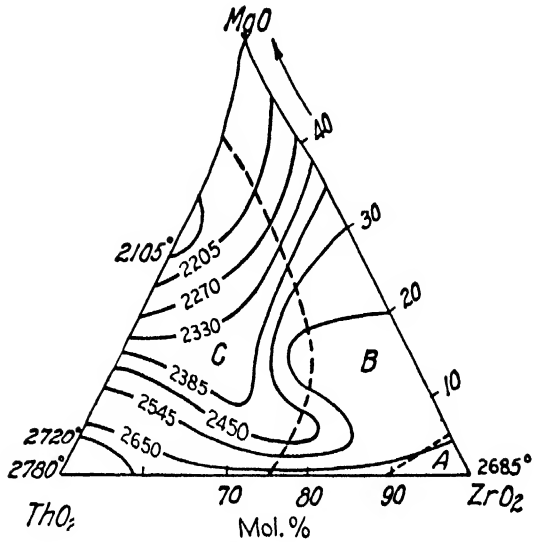


FIG. 225. Melting isotherms of system MgO–ThO_2–ZrO_2; *A* = monoclinic ZrO_2, *B* = cubic mix crystal, *C* = two cubic mix crystals. (*Otto Ruff, F. Ebert, and W. Loerpabel, Z. anorg. u. allgem. Chem.*, **207**, 309, 1932.)

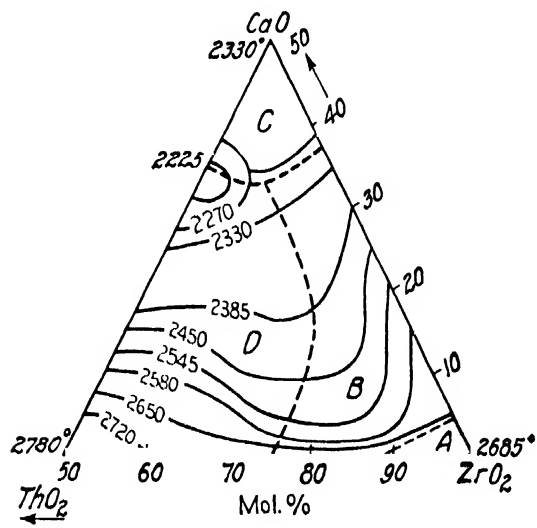


FIG. 226. Melting isotherms of system CaO–ThO_2–ZrO_2; *A* = monoclinic ZrO_2, *B* = cubic mix crystal, *C* = cubic mix crystal + $CaZrO_3$, *D* = two cubic mix crystals (miscibility gap). (*Otto Ruff, F. Ebert, and W. Loerpabel, Z. anorg. u. allgem. Chem.*, **207**, 309, 1932.)

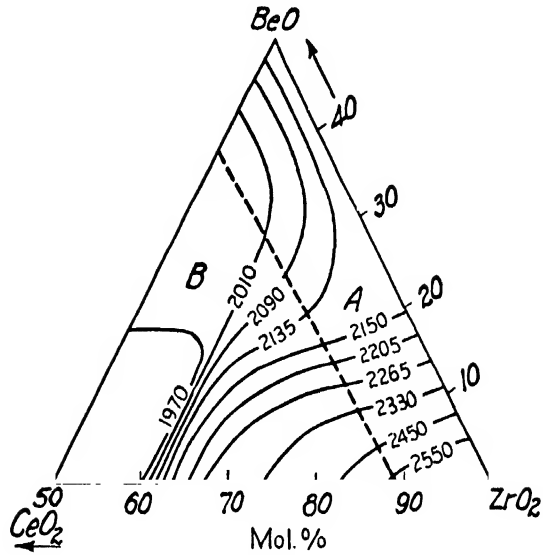


FIG. 227. Melting isotherms of system BeO–CeO_2–ZrO_2; *A* = monoclinic ZrO_2, *B* = cubic mix crystal. (*Otto Ruff, F. Ebert and W. Loerpabel, Z. anorg. u. allgem. Chem.*, **207**, 310, 1932.)

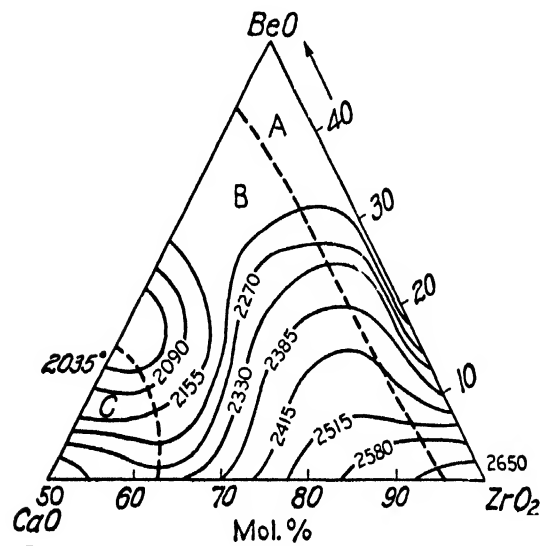


FIG. 228. Melting isotherms of system BeO–CaO–ZrO_2; *A* = monoclinic ZrO_2, *B* = cubic mix crystal, *C* = cubic mix crystal + $CaZrO_3$. (*Otto Ruff, F. Ebert, and W. Loerpabel, Z. anorg. u. allgem. Chem.*, **207**, 310, 1932.)

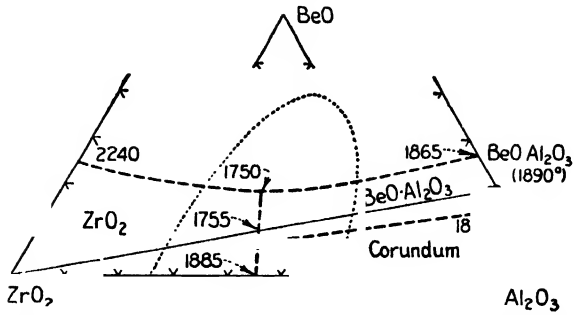


FIG. 229. System BeO–Al_2O_3–ZrO_2. (*Geller, et al., see p. 303 of reference of Fig. 231.*)

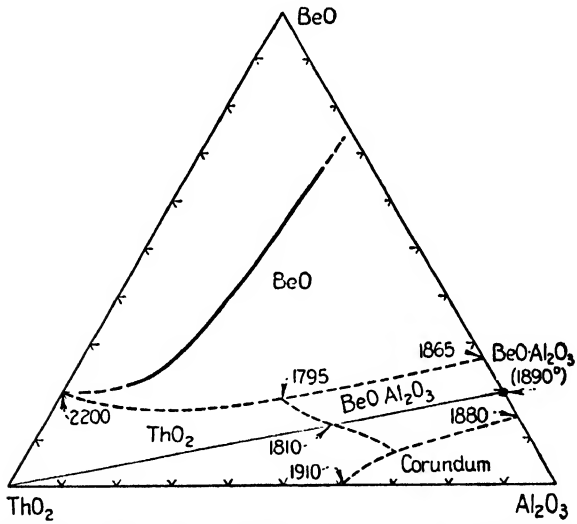


FIG. 230. System BeO–Al_2O_3–ThO_2. (*Geller, et al., see p. 298 of reference of Fig. 231*)

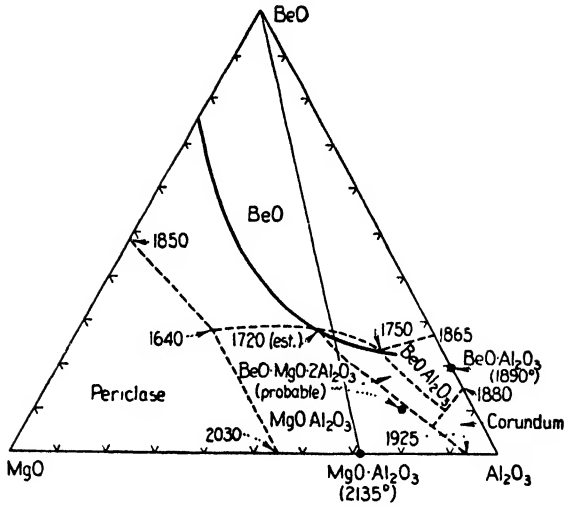


FIG. 231. System BeO–MgO–Al_2O_3. (*R. F. Geller, P. J. Yavorsky, B. L. Steierman, and A S. Creamer, J. Research Nat. Bur. Standards*, **36**, (3) 289, 1946; *R. P.* 1703.)

Pt	Crystal phases	CaO	MgO	Al_2O_3	Temp
A	C, M	67.0	33.0	..	2300
B	M, MA	.. .	45.0	55.0	2030
C	MA, A	.. .	2.0	98 0	1925
D	C, C_3A	59.0	. .	41 0	1535
E	C_3A, C_5A_3	50.0	....	50 0	1395
F	C_5A_3, CA	47.0	....	53.0	1400
G	CA, CA_6	33 5	....	66.5	1590
H	CA_6, A	24.0	....	76.0	1700
1	M, C, C_3A	51.5	6.2	42 3	1450
2*	M, C_3A, C_5A_3	46.0	6.3	47.7	1345
3*	M, C_5A_3, CA	41 5	6.7	51.8	1345
4	M, MA, CA	45.7	6 9	52 4	1370
5	MA, CA, CA_6	33 3	3.5	63.2	1550
6	CA_6, MA, A	21 0	5.0	74.0	1680
$5CaO·3Al_2O_3$		47 8	...	52 2	1455
$CaO·3Al_2O_3$		35.4	....	64.6	1600
$3CaO·5Al_2O_3$		24.8	....	75 2	1720
$MgO·Al_2O_3$		....	28.4	71.6	2135
$3CaO·Al_2O_3$		62.2	....	37.8	1535
Periclase		...	100 0	.. .	2800
Lime		100.0	....	..	2570
Corundum		.....	.....	100.0	2050

* Eutectic.

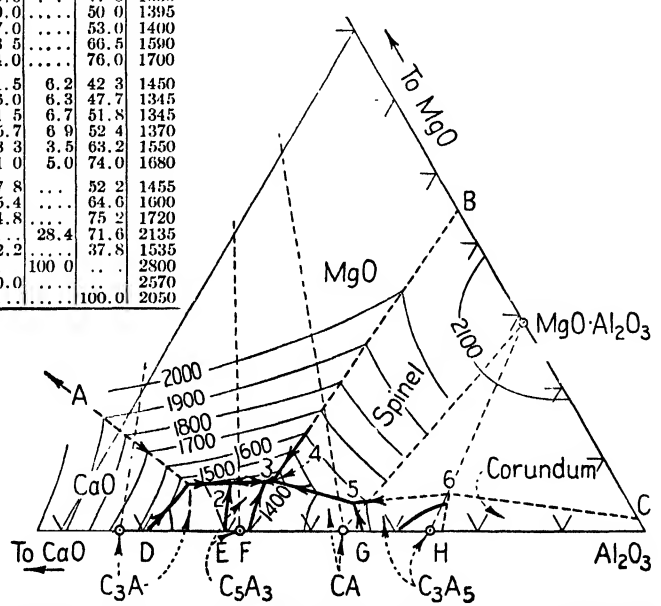


FIG. 232. System CaO–MgO–Al_2O_3; C = CaO, M = MgO, A = Al_2O_3. (*G. A. Rankin and H E. Merwin, Z. anorg. u. allgem. Chem.*, **96**, 309, 1916.)

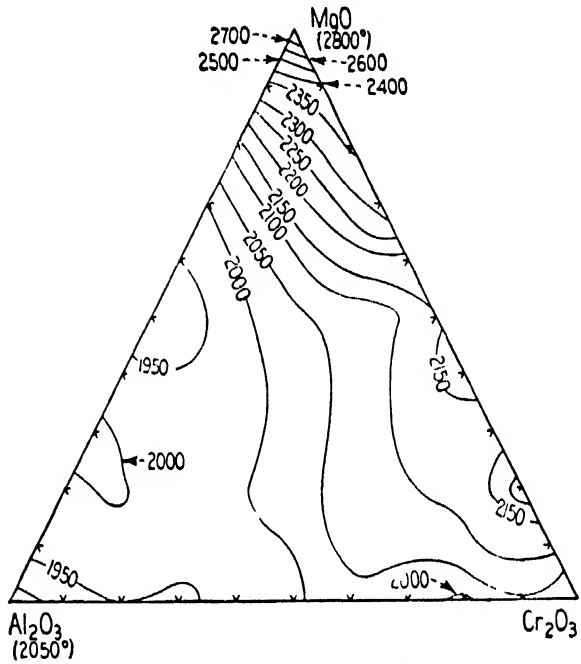


FIG. 233. Melting isotherms of system MgO–Al_2O_3–Cr_2O_3. (*W. T. Wilde and W. J. Rees, Trans. Brit. Ceram. Soc.*, **42**, 127, 1943.)

CHAPTER XIV

LOAD-BEARING CAPACITY OF REFRACTORIES

1. Mechanism of Load Failure. *Flow Characteristics of Glass.* The flow properties of a heated glass fiber are shown in Fig. 234, in which the elongation is plotted against time for a single load. It will be noted that the flow starts in rapidly but soon decreases until it reaches a constant rate. If the straight portion of the curve is projected back to the zero time axis, the value S_1 is obtained, which represents the elastic strain. If, at time t_1, the load is removed, the glass will contract rapidly at first and

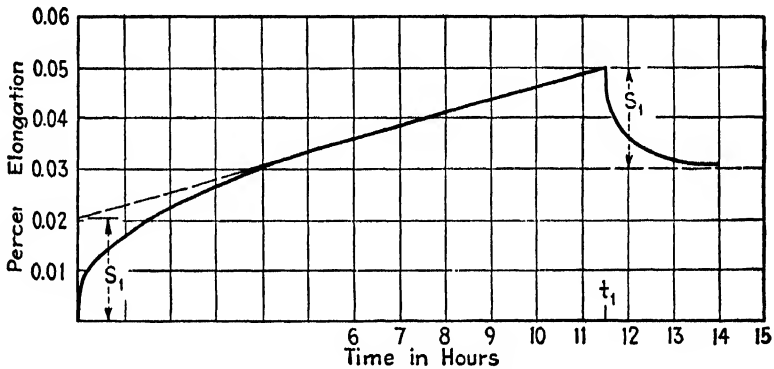


FIG. 234. Flow of heated glass.

then more slowly until it reaches a fixed length. The amount of contraction is equal to S_1, or the original elastic effect. The heated glass is a truly viscous material; for if the steady rate of flow is plotted against stress as shown in *A* of Fig. 235, a straight line passing through the origin results.

The mechanism of flow in glass can perhaps be made clearer by considering a mechanical model, the motion of which reproduces the glass flow with considerable exactness. This model, shown in Fig. 236, consists of the spring *A*, which represents the elastic effect in the glass but is restrained from reaching instant equilibrium by the dashpots *B*, representing the restraining force or internal friction of the glass. The steady flow of the glass is represented by the motion of the dashpot *C*; the weight *W* provides the extension force.

Flow of Crystals. The flow of single crystals of nonmetals at elevated temperatures has not been studied with any great care. It is believed that

the single crystal has a definite yield point but deforms plastically below the melting temperature. Research on single crystals is complicated by the fact that some distortion occurs, probably along the slip planes, until there is no longer a single crystal and we must consider the system as many similarly oriented small crystals. A still greater departure from a single crystal is a system of small crystals with random orientation, which gives, in effect, the conditions of an isotropic medium. Here again, we have little information on the flow properties.

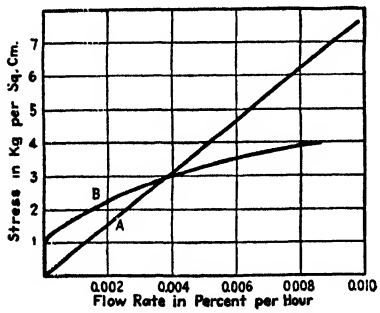


FIG. 235. Flow characteristics of a viscous material (*A*) and an elastico-plastic material (*B*).

Flow of a Mixture of Crystals and Glass. This mixture, which is a normal characteristic of most refractory materials, has been studied to a considerable extent. Such mixtures are elastico-plastic materials, similar in flow characteristics to plastic metals; *i.e.*, if the steady rate of flow is plotted against stress, a line results that does not pass through the origin but indicates a certain minimum stress necessary to initiate flow, as shown in curve *B* of Fig. 235, a characteristic typical of all plastic materials. The time-elongation curve, however, is very similar to that for a glass, as indicated in Fig. 237 for a porcelain. This shows the initial portion of rapid flow and later the gradual conformity to a uniform rate. It is characteristic of almost all refractory materials that the rate of flow soon after the load is applied is much greater than after a uniform condition has been reached. Also it should be remembered that in plastic flow, the rate of flow is roughly proportional to the fourth power of the stress and not the first power as in viscous flow.

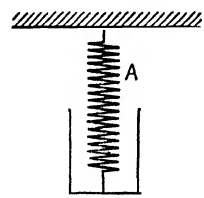


FIG. 236. Model simulating the flow in glass.

In Fig. 238 is shown a more or less idealized type of flow diagram for a refractory material at various temperatures.

The flow relations in an elasticoviscous material may be clarified by a mathematical discussion.

Let S_t = the total flow of the specimen

S_e = the elastic portion of the flow

S_1 = the total elastic flow under the external force F

Now the force acting at any instant to cause elastic flow is

$$F_1 = F(S_1 - S_e)$$

That is, at the start of flow, $F_1 = F$, whereas at the condition of equilibrium flow $F_1 = 0$.

The retarding force restraining the elastic flow is given by

$$F_2 = k\frac{dS_c}{dt}$$

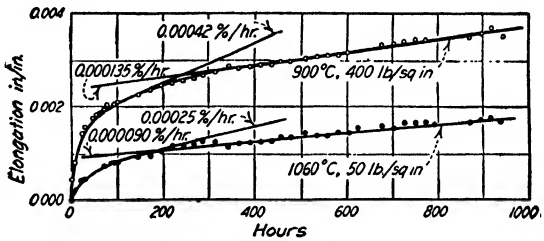


FIG. 237. Plastic flow of heated porcelain.

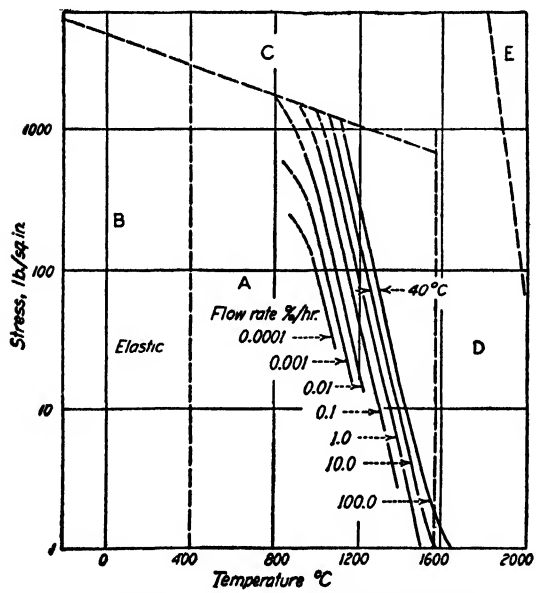


FIG. 238. The flow field of a porcelain.
A = field of plastic flow
B = field of elastic flow
C = field of instant breaking
D = field of viscous flow
E = field of turbulent flow

But any time

$$F_1 = F_2$$

or

$$F(S_1 - S_e) = k\frac{dS_e}{dt}$$

Solving for S_e we obtain

$$S_e = S_1(1 - e^{Ft/k})$$

The viscous flow is

$$S_v = k_1 t$$

Then

$$S_t = S_v + S_e$$
$$S_t = k_1 t + S_1(1 - e^{Ft/k})$$

This expression represents the flow relation of Fig. 234 and the motion of the model of Fig. 236. After a period of time, the second term becomes zero and the flow is steady.

In the case of elastico-plastic flow, we can set up the expression for the elastic flow as

$$F(S_1 - S_e) = k_2(dS_e/dt)^n$$

and for the plastic flow as

$$S_p = k_3 t$$

where S_p = the plastic flow
$n = \frac{1}{4}$ (approximately)

The solution of these equations gives an expression for the total flow of

$$S_t = k_3 t + S_1\left(1 - \sqrt[3]{\frac{1}{3F^4S_1^3 + 1}}\right)$$

Reference should be made to the excellent series of papers on the flow of refractories by Clews and his coworkers.[48,49,52]

2. Method of Measurement. *ASTM Load Test.* The load resistances of refractories are almost invariably measured with a compression specimen, which is heated under a definite schedule and the amount of deformation determined at the end of the test. However, tension[30,33,42,47] and torsion[31,32,41] tests have been made. A typical example of the compression tests is the ASTM standard test, which may be quoted as follows:

STANDARD METHOD OF TEST FOR REFRACTORY MATERIALS UNDER LOAD AT HIGH TEMPERATURES

ASTM Designation: C 16–41[1]

ISSUED AS TENTATIVE, 1939: ADOPTED, 1941

This Standard of the American Society for Testing Materials is issued under the fixed designation C 16; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision.

1. Scope. This method of test covers the procedure for determining the resistance to deformation of fireclay refractories, when subjected to a specified compressive load at a specified temperature for a specified time.

2. Apparatus. *a.* The apparatus shall consist essentially of a furnace and a loading service. It may be constructed in accordance with Fig. 239 or its equivalent.[2]

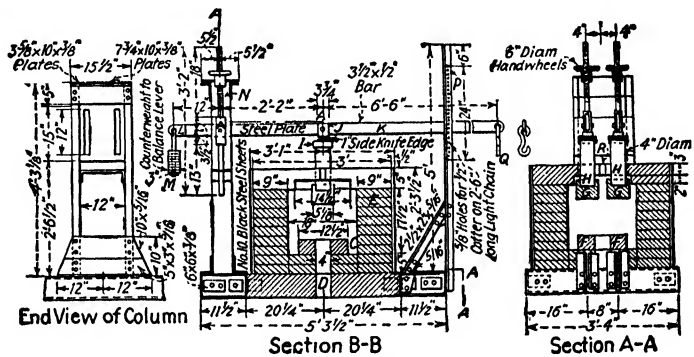


FIG. 239. Standard load-test furnace.

When gas or oil fuel is used, the furnace shall be of such form that the temperature is substantially uniform in all parts of the furnace. Two burners shall be used. These shall be capable of individual control and located to produce a tangential flame that will not impinge on the specimens or on the thermocouple protecting tubes.

b. The temperature shall be measured either with calibrated platinum–platinum-rhodium thermocouples, each encased in a protection tube with the junction not more than 1 in. (25 mm) from the center of the side or edge of each specimen farthest from the center of the furnace, or with some form of pyrometer that has been calibrated against a thermocouple in the furnace. A recording form of temperature indicator is recommended. If the optical pyrometer is used, obser-

[1] ASTM Standards are subject to revision. The Society's headquarters, in Philadelphia, may be consulted for the latest information.

[2] This standard, as adopted in 1941, recommends furnaces of three types, viz., the direct-load-type, gas- or oil-fired; the direct-load-type, electrically heated; and the lever-type load test furnace. Only the last is here illustrated.

vations shall be made by sighting into refractory tubes having closed ends and in the same relative positions to the test specimens as those specified for the thermocouples.

3. Test Specimen. *a.* The test specimen shall consist of a minimum of two 9 by 4½ by 2½ in. straight refractory brick, or specimens of this size cut from larger shapes, utilizing as far as possible existing plane surfaces.

b. If necessary, the ends of the specimen shall be ground so that they are approximately perpendicular to the vertical axis.

TABLE 72. TIME-TEMPERATURE SCHEDULES FOR HEATING THE TEST FURNACE

NOTE: All temperatures shall be maintained within ±10°C of those prescribed in this table, and the averages of the temperatures attained shall equal those specified.

Time		Temperatures for various heating schedules, °C, fireclay brick			Tentative schedule of temperatures, °C	
Hours	Minutes	Schedule No. 3, super duty	Schedule No. 2, high heat duty	Schedule No. 1, intermediate heat duty	Schedule No. 4, silica brick	Schedule No. 5, basic and neutral brick
After 1	0	560	500	500	119	500
	15	680	620	595	154	620
	30	800	720	685	193	720
	45	900	815	770	232	815
After 2	0	990	900	850	280	900
	15	1070	980	920	335	980
	30	1140	1045	990	413	1045
	45	1200	1100	1050	552	1100
After 3	0	1250	1150	1100	690	1150
	15	1290	1195	1145	830	1195
	30	1330	1235	1185	955	1235
	45	1370	1270	1220	1090	1270
After 4	0	1400	1300	1250	1205	1300
	15	1430	1330	1275	1315	1330
	30	1450	1350	1300	1400	1350
	45	1450	1350	1300	1455	
After 5	0	1450	1350	1300	1480	To failure
	15	1450	1350	1300	To failure	at 56°C
	30	1450	1350	1300	at 56°C	per hr
	45	1450	1350	1300	per hr	
After 6	0	1450(end)	1350(end)	1300(end)		

c. The test specimen shall be measured before testing, four observations being made on each dimension (length, width, and thickness) at the center of the faces to within or minus 0.02 in. (0.5 mm). The average dimensions shall be recorded, and the cross section calculated.

4. Setting the Test Specimen. The test specimen, set on end, shall occupy a position in the furnace so that the center line of the applied load coincides with the vertical axis of the specimen as indicated in Fig. 239 and shall rest on a block of some highly refractory material, neutral to the specimen, having a minimum expansion or contraction. (Recrystallized silicon carbide brick have been found satisfactory for this purpose.) There shall be placed between the specimen and the refractory blocks a thin layer of highly refractory material such as fused alumina or silicon carbide, which has been ground to pass a No. 20 (840μ) ASTM sieve (equivalent to mesh No. 20 of the Tyler standard series). At the top of the test specimen a block of similar highly refractory material should be placed, extending through the furnace top to receive the load.

NOTE: Gross errors which may more than double the deformation will result if the specimen is not set perpendicular to the base of the support or if the load is applied eccentrically.

5. Procedure. *a. Loading.* The gross load to be applied shall be calculated from the average cross section of the original specimen as determined in Sec. 3*c*. A load of 25 lb per sq ft (1.765 kg per sq cm) shall be used.

b. Heating. The rate of heating shall be in accordance with the requirements of Table 72 and the time-temperature curves shown in Fig. 240 which give the rate and time of heating required for different classes of refractory materials. The temperature shall not vary more than ± 10°C from the specified temperature.

c. Furnace Atmosphere. The furnace shall be operated with an oxidizing atmosphere above 800°C.

d. Completion of Test. At the expiration of the time of heating, the supply of heat shall be stopped and the furnace allowed to cool by radiation to 1000°C, or lower, before the load is removed and the specimens examined. When the test specimens have cooled to room temperature, they shall be remeasured for length in accordance with Sec. 3*c*, and the average deformation shall be recorded and reported to the nearest 0.5 per cent of the original length.

NOTE: It is recommended that a photograph be made of the specimen before and after testing, since these will yield useful information.

The ASTM load test has been developed over a long period to fit best the needs of the manufacturer and the user of refractories and is particularly useful in control testing. As discussed later, it does not give information particularly suited to the need of the designer.

European Load Tests. In Europe, the load test is generally carried out on smaller specimens, *i.e.*, cylinders approximately 1 in. in diameter and 1 in. high. This method is preferred because the temperature can be made more uniform over the specimen and the furnace is smaller and more easily

controlled. An excellent furnace of this type is described by Swallow.[50] On the other hand, such a small specimen may not represent accurately the structure of a coarse-grained brick, and the specimens are so short that the precision of measuring the elongation is somewhat less than with the larger specimens. However, there are certain advantages with each type of specimen; and with carefully made tests, either should give reliable results. An excellent discussion of the load test is given in the references.[34,39]

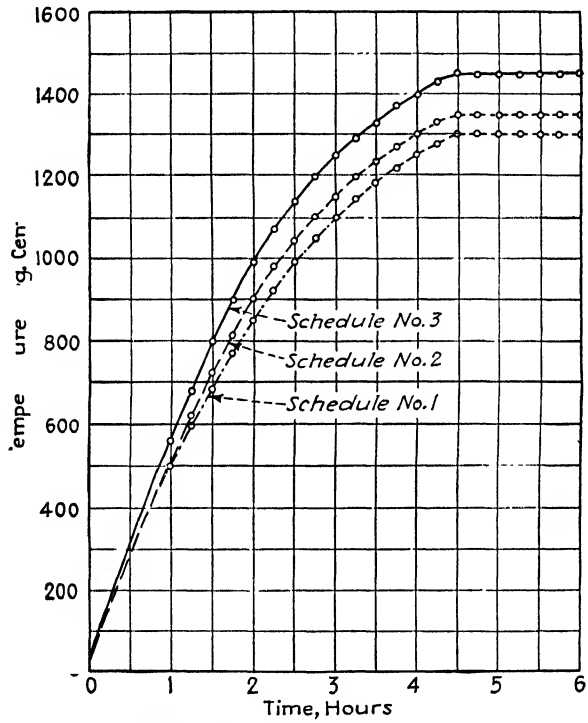


FIG. 240. Time-temperature curve for load test.

Long-time Creep Tests. Recently, some work has been carried out on the load testing of refractories in the same way that creep tests are made with metals;[45] *i.e.*, the refractory is heated to a uniform temperature and then loaded for a sufficient length of time to establish a uniform rate of flow. A furnace that is heated by electric globars to the necessary temperature for carrying out this test is shown in Fig. 241. The length of the specimen not only is measured at the end of the run but is measured every day with a pair of telescopes sighting on the ends of the specimen in order to determine a time-elongation curve. Figure 242 shows such a series of

curves for a firebrick run in this way; and in Fig. 243, the flow rates are plotted against load on logarithmic paper. It is felt that for design purposes, the long-time tests are much preferred to the short-time tests previously described. Whether or not the shorter tests give accurate com-

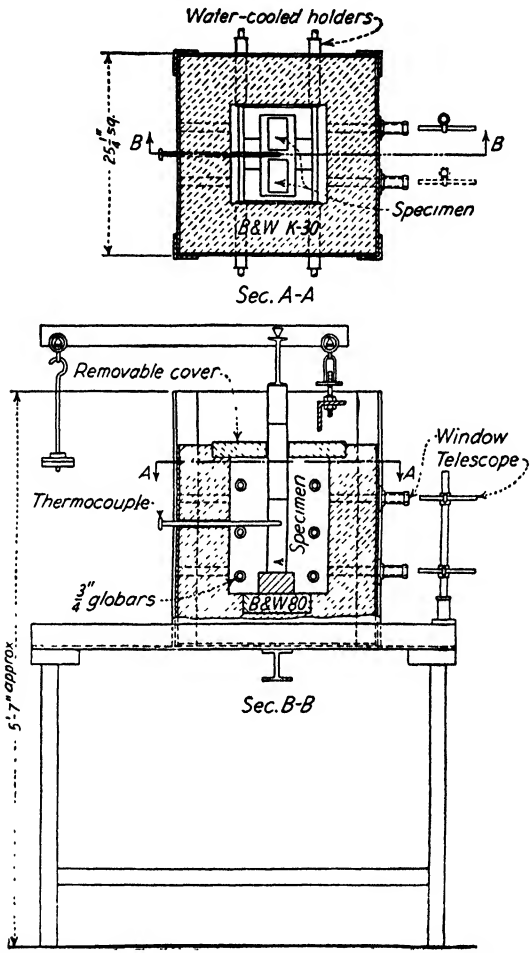


FIG. 241. Electrically heated load test furnace. (*J. Am. Ceram. Soc.*)

parisons between various bricks cannot be determined until more long-time tests have been made to reproduce more nearly actual conditions.

Considerable interest has been shown in the use of pure, sintered refractories for high-temperature structural parts such as described in Chap. XII. Both hot tensile strengths and tensile creep values have been

obtained on a number of materials. Most of the tests have been made on special specimens mounted in refractory holders with provisions for axial loading, which is of the utmost importance when dealing with brittle materials. While most of the testing has been done in a standard tensile machine, Towers[56] has developed a pneumatic type that seems to give

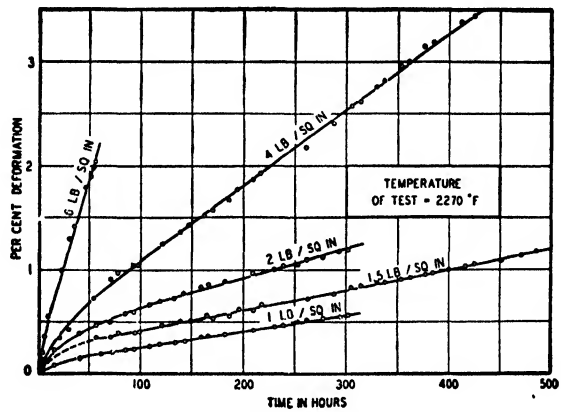


FIG. 242. Time-elongation curve for a firebrick. (*J. Am. Ceram. Soc.*)

unusually consistent results. The series of papers by Clews and his collaborators[48,49,52] gives an excellent discussion of the flow of refractories, while the best data on tensile creep at high temperatures are those reported by Burdick, Moreland, and Geller.[61]

Recently, there has been developed in the Ceramic Laboratory of the Massachusetts Institute of Technology a torsion creep test for refractories of a unique character,[60] as the optical system is in the furnace. The

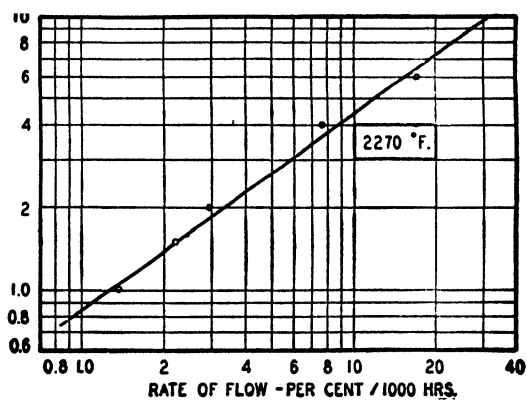


FIG. 243. Flow rate *vs.* load. (*J. Am. Ceram. Soc.*)

general plan is shown in Fig. 244. The specimen *a* is put under a steady torsional stress by the torque wheel *f* and the weight *g* through the refractory holders *e*. At the end of the gage length of the specimen are cemented two concave sapphire mirrors, *b*, ⅛ in. in diameter. Light from lamps *c* are focused by these mirrors on the ground-glass scale *d*, so that any twist in the gage length shows up as a separation of the light spots. The screw *i* in the nut *j* moves the arm *h* by the micrometer dial *k* to calibrate the scale *d*. This method can be used up to at least 1300°C (about 2370°F)

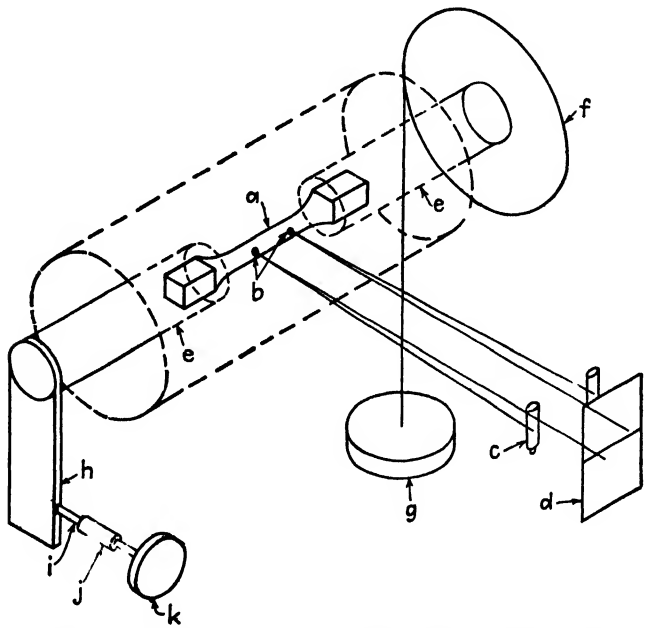


FIG. 244. A torsion creep furnace with a sapphire optical system.

with a precision of ±0.001 deg. It should be noted that the holders do not have to be rigidly attached to the specimen, as slippage does not affect the optical readings. This method has many advantages over the tensile test because of its much greater precision in determining low flow rates.

3. Load Values for a Number of Refractories. In Table 73 will be found the comparative load values for a number of fireclay brick that have been tested in the ASTM type load test as published by the Refractories Institute.

Table 74 shows load values for a number of special refractories run in the ASTM furnace but at the schedule shown in Fig. 245 in order to bring all of them down to give a direct comparison.

Only recently[46] have any values been available on the load values of insulating firebrick. The bricks shown in Table 75 are representative of those on the market at present. Their load value together with those of two second-quality fireclay brick are given in Table 76 when heated on the schedule shown in Fig. 246. It is interesting to notice that some of the insulating firebrick, even though they have a porosity of around 80 per

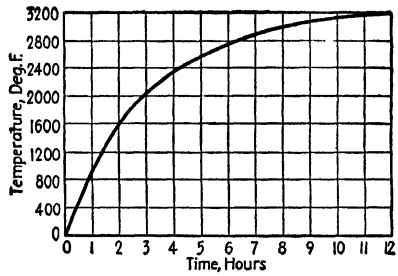


FIG. 245. Load-test schedule for special bricks.

TABLE 73. LOAD-BEARING CAPACITY OF FIRECLAY BRICK

Method of manufacture	Brand No.	Pyrometric cone equivalent	Subsidence, per cent, at 1350°C. (2462°F.) load test 25 lb. per sq. in.	Chemical composition					
				Silica	Alumina	Iron oxide	Titania	Lime and magnesia	Combined alkalies
	A	19	Failed	68.88	24.03	2.57	1.24	0.92	2.01
	B	31	12.70	55.20	40.00	2.40	2.00	0.80	1.60
	C	32	3.40	61.18	35.05	1.91	1.04	0.61	0.71
Dry press...	D	32	10.50	54.22	38.58	1.86	2.26	0.87	2.34
	E	32–33	3.60	54.08	40.97	2.34	1.89	0.40	1.42
	F	33	6.90	53.00	42.70	1.70	2.04	0.70	0.80
	G	33	2.60	52.47	42.70	1.56	1.97	0.48	0.62
	H	35–36	0.90	33.54	59.64	1.76	2.34	0.54	1.55
	I	31–32	1.30	73.81	21.69	1.85	0.90	0.40	0.66
	J	30–31	4.00	68.24	28.29	1.55	0.66	0.94	0.32
Stiff-mud....	K	30–31	5.60	60.04	33.22	1.83	0.99	1.20	2.32
	L	32–33	5.60	57.44	36.88	2.14	1.80	0.75	0.72
	M	32–33	3.90	52.66	38.57	2.28	2.53	0.96	2.64
	N	32–33	1.85	52.73	43.20	2.29	1.02	0.44	0.37
	P	29–30	4.95	75.96	21.46	1.12	1.10	0.54	0.70
	Q	27–28	2.62	70.00	25.00	1.20	1.00	0.50	2.30
	R	30–31	9.86	65.28	28.47	1.77	0.56	0.83	1.79
Hand-made..	S	31–32	3.30	60.08	34.04	1.40	2.16	0.63	1.84
	T	32	8.43	48.42	44.33	3.58	1.70	0.90	1.52
	U	32	5.95	51.30	42.30	2.23	2.28	0.47	1.55
	V	33–34	10.90	42.20	49.98	3.18	2.40	0.85	1.47

TABLE 74. SPECIAL REFRACTORIES

Type	Temperature for 10 per cent deformation		Test†
	°C	°F	
Commercial fused alumina	1716	3121	
Fused alumina, Norton RA 1190 35 (99 per cent + Al_2O_3)	1925[55]	3497	10 psi: 10°C per min
Chrome, commercial	1404	2559	
Chrome-magnesite (German, av fig.)	1640[51]	2980	28 psi
Kaolin (B & W K-80)	1593	2899	
Magnesite (sintered Grecian)	1400*	2552	
Magnesite, fused (Norton LM 171-35)	2240[55]	4064	10 psi: 10°C per min
Mullite, dense	1727	3140	
Silica, commercial	1646*	2985*	
Spinel	1510*	2750*	
Zirconia (clay-bonded baddeleyite)	1376	2509	
Zirconia, fused, lime stabilized, Norton LZO 172-35	2200[55]	3992	10 psi: 10°C per min

* Sheared.

† Unless noted tested under 25 psi at temperature rise shown in Fig. 245.

TABLE 75. TEST DATA ON COMMERCIAL INSULATING FIREBRICK

Brand No.	Use limit, °F	Weight, lb per 9 in. straight	Modulus of rupture, psi	Cold crushing strength, psi
A	2000	1.72–1.82	95	120
B	2000	2.21–2.75	197	172
C	2000	1.64	71	104
D	2000	2.27–2.32	107	559
O	2000	1.88	106	176
E	2200	1.87–1.96	165	193
F	2200	2.71–3.07	224	377
G	2200	2.27	129	208
N	2200	2.44	66	235
I	2500	2.40–2.63	196	248
J	2500	2.76	251	408
K	2600	2.30–2.50	133	128
L	2600	2.68–2.80	203	372
S	2600	2.40	127	196
M	2800	2.42 2.48	140	150
T	2900	2.90	235	220

TABLE 76. LOAD-TEST RESULTS

Brand No.	Percentage at 1900°F.		Percentage at 2000°F.			Percentage at 2100°F.			Percentage at 2200°F.			Percentage at 2300°F.		
	10 lb.	25 lb.	10 lb.	25 lb.	40 lb.	10 lb.	25 lb.	40 lb.	10 lb.	25 lb.	40 lb.	10 lb.	25 lb.	40 lb.
A			0.1	0.1	0.1	0.0	0.2	0.3	0.4	0.7	1.1	1.1	2.7	Failed
B	0 1	1.6	0.6	8.3										
C	0.1	Failed	1.0	Failed										
D			0.9	1.3	2.5	2.5	2.9	4.9	3.8	Failed				
O			Failed											
E			0.1	0.0	0.1	0 0	0.1	0.2	0.1	0.1	0.4	1.6	2.6	Failed
F			0.1	0.4	1.8	0.2	2 5	7.6	2.5	Failed				
G			0.1	1.8	7.6	1.5	Failed							
N			Failed											
I			0.1	0.8	1.2	0.2	2.0	Failed	1.9	Failed				
J				0.2	0.2	0.0	0.2	0.7	0.1	1.7	Failed			
K						0.3	0 4	0.6	0.3	1.0	2.9	1.4	Failed	
L			0.0	0.2	0.4	0.1	0.9	1.6	0.9	1.2	5.5			
S			0.1	0.1	0 2	0.2	0 3	0 8	0 4	2.9	8.2			
M						0 0	0.4	0 9	0 1	1 0	3.9	0.4	1 3	Failed
T				0.1	0 2	0 2	0 1	0.4	0 2	0.4	0.6	0.3	0.8	0.9
1											0.4			Failed
2											0.2			

cent, give a resistance to load superior to the second-grade fireclay brick with a porosity of around 25 per cent.

4. Factors Influencing the Load-bearing Capacity of Refractories. In general, it may be said that the load-bearing capacity of a refractory is directly influenced by the amount and viscosity of the glassy phase. Anything that can be done to diminish the amount of glass or raise its viscosity will increase the resistance to flow. This can be accomplished by adding

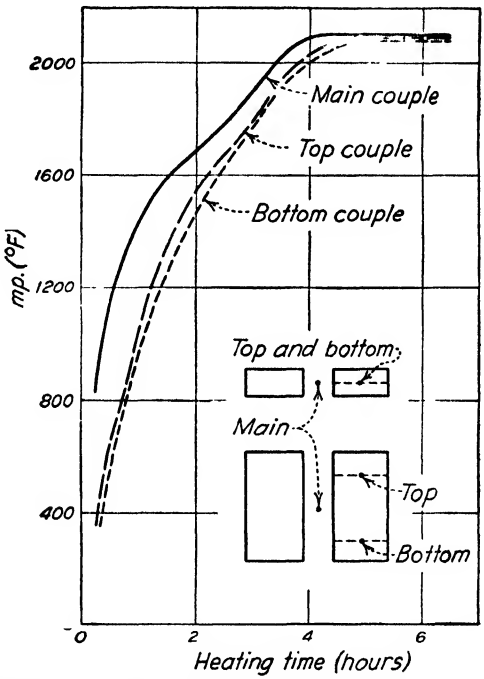


FIG. 246. Temperature *vs.* heating time during load testing of insulating firebrick. (*J. Am. Ceram. Soc.*)

to the refractory a material that will form from the glass a more viscous material or a material containing more crystals. For example, a chrome brick containing silica as an impurity may have a comparatively low load value; whereas if the proper amount of magnesite is added to the brick, it will form the crystalline magnesium ortho-silicate, forsterite, which will greatly increase the load-bearing value of the brick. Also, an increase in firing temperature will generally increase the load-bearing capacity because it distributes the glassy phase more thoroughly and permits it to absorb crystallizing elements. This is shown in Table 77, which lists a number of commercial firebricks that were tested as they came from the kiln and then after refiring at a higher temperature.

CHAPTER XV

SPALLING

1. Introduction. Spalling is usually defined as a fracture of the refractory brick or block resulting from any of the following causes:

1. A temperature gradient in the brick, due to uneven heating or cooling, that is sufficient to set up stresses of such magnitude as to cause failure.
2. Compression in a structure of refractories, due to expansion of the whole from a rise of temperature, sufficient to cause shear failures.
3. Variation in coefficient of thermal expansion between the surface layer and the body of the brick, due to surface slag penetration or to a structural change in service, great enough to shear off the surface layer.

Many consider only the first type as true spalling. It is undoubtedly the predominating effect in refractories such as silica, magnesite, and chrome. As this type is caused by the inherent properties of the refractory, it offers a good opportunity for careful analysis. The second type of spalling is almost always due to poor furnace design, and the refractory itself can seldom be blamed. The third type can be minimized by using bricks burned higher than their subsequent operating temperature and by preventing slag penetration in so far as is possible.

The spalling properties of refractories cannot be consistently improved until we know the true mechanism of spalling. Although the study of stresses and fractures in brittle material is by no means well understood, light has been thrown on the matter in recent years. This work has been extended by Booze[11] and Phelps,[16] Green,[17] Preston,[15] numerous researches at the National Bureau of Standards, and by Endell in Germany.

2. Temperature Stresses in Solids. It may be of interest to examine first the distribution of stress in an elastic solid when its surface is heated or cooled. It is rather surprising that there has been so little recognition of the difference in stresses resulting from heating as differentiated from cooling. As will be shown later, the stresses as well as the fracture are quite different in the two cases. An investigation, therefore, has been carried out by the photoelastic method to determine the stresses occurring in various objects when suddenly heated and cooled at the surface.

Photoelastic Method. The method of studying stresses in various structures by photoelasticity has recently been used to a considerable extent in determining the distribution of stress in objects where a direct computa-

tion is impossible. For example, valuable studies have been made of the stresses in hooks, eyebolts, ships' hulls, and gear teeth, although it is believed that very little work has been previously carried out on the measurement of temperature stresses by this method.

Photoelastic models must be made from a transparent isotropic medium. In this case, clear bakelite was selected because of its high stress–optical coefficient.

Polarized light is passed through a plane specimen, which becomes double refracting under stress and retards the two wave systems according to the values of the principal stresses p and q. The two wave systems interfere when passed through an analyzer and give isochromatic bands proportional to the difference $p - q$. The isochromatic lines are also lines of principal shear, for the principal shear stress at any point is equal to one-half the difference of the two principal stresses. The separate values of p and q can be determined by repeating the observations with circularly polarized light, which shows the isoclinic lines, or lines of equal direction of principal stresses. The values of p and q can be calculated from the isoclinic and isochromatic lines, the boundary conditions, and the constants of the material. It should be emphasized that this method applies only to a plane object.

Temperature Stress Tests. The first model to be studied was a disk. This disk was carefully maintained at 50°C (122°F); then the circumference was suddenly heated to 100°C (212°F) by steam, and the resulting development of stresses watched until they had reached a maximum value, which required about 45 sec. The experiment was then repeated by suddenly chilling the circumference from 50°C (122°F) to 0°C (32°F) by means of ice water, and the stresses were similarly studied. In Fig. 247 are given the magnitudes and directions of the shear and resultant stresses under these conditions.

It will be observed that when the circumference is suddenly heated, tangential compression of considerable magnitude is developed near the surface but the center of the disk is under a slight tension having an equal magnitude in all directions. The radial stresses are zero at the circumference but increase slowly toward the center. On the other hand, when the circumference is cooled, the surface is under considerable tension and the center of the disk is under light compression. In both cases, the shear stresses are the same and reach a maximum at the circumference. Their direction is everywhere at 45 deg to the radii.

The next model tested was a brick heated on the end. The stresses are shown in Fig. 248 in the same way as for the disk. On heating, a compression maximum occurred at the center of the end; but on cooling, this was changed to a tension. It will be noted that the directions of the shear

stresses are approximately 45 deg to the surface everywhere and are a maximum at the center of the end.

In the case shown in Fig. 249, the model brick was heated at the end and about one-third of the way up the side. A somewhat different type of stress distribution resulted, for the increase in stresses at the sides causes

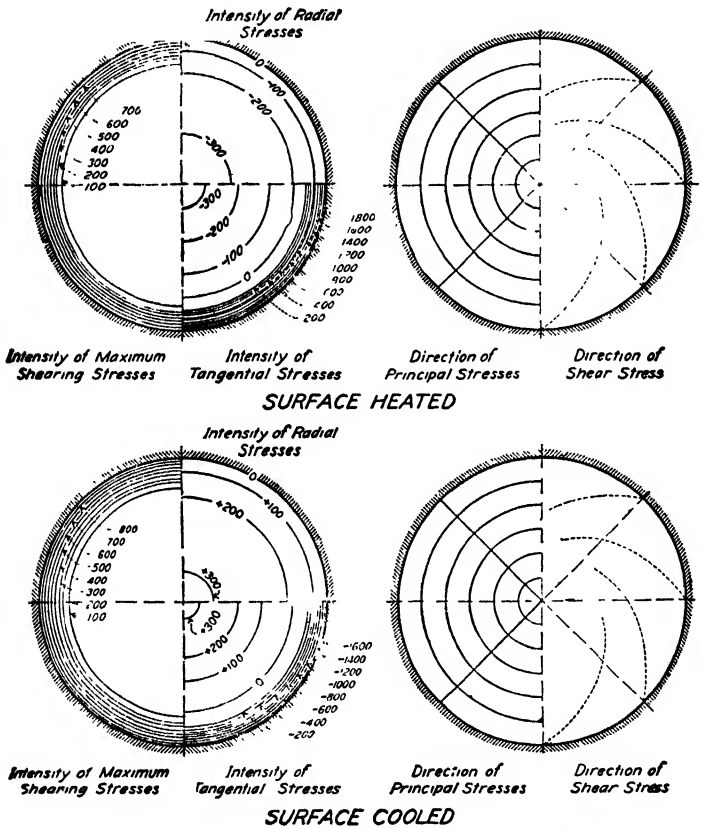


FIG. 247. Stresses in a disk. (*J. Amer. Ceram. Soc.*)

the stresses at the end to decrease. It will be noted that at the corners, the shear lines are curved and follow the isothermals closely.

Figure 250 shows a model representing a brick in a wall when this wall is heated and cooled at the surface. The isothermals will then be parallel to the heated surface. It will be noted that the resultant normal stresses are nearly parallel and perpendicular to the surface of the wall and that the shear stresses are at 45 deg to them.

Conclusions. We may conclude from the preceding results that

1. The stresses set up in a solid by suddenly heating the surface through a certain temperature interval are of the same order but of opposite sign from those set up by cooling the surface through the same temperature range.
2. No high tensile stresses are developed on sudden heating.
3. The maximum shearing stresses are equal to one-half the maximum resultant stresses.
4. The stresses are generally low at the corners and interior of the specimen but reach their highest value along the heated sides at a distance from the corners.

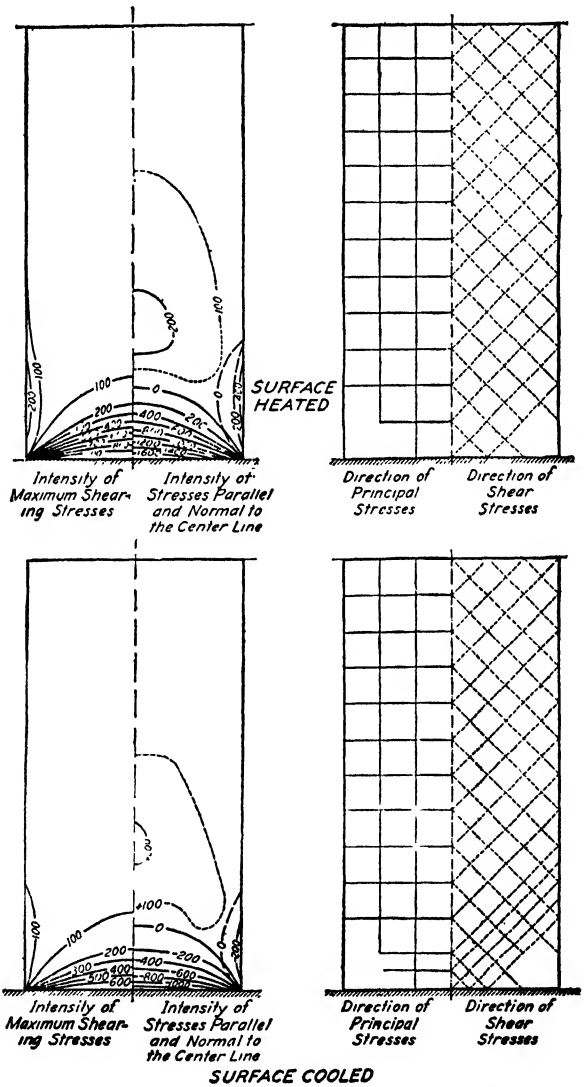


FIG. 248. Stresses in a brick heated at one end. (*J. Amer. Ceram. Soc.*)

3. Study of Cracks Developed in Spalling. In order to correlate the types of cracks formed in the material when heated and cooled, with the stress distribution previously determined, a number of spheres and bricks were made up with a fine-grained, porcelain-like structure in order to make spalling occur readily. These objects were gradually heated to 900°C

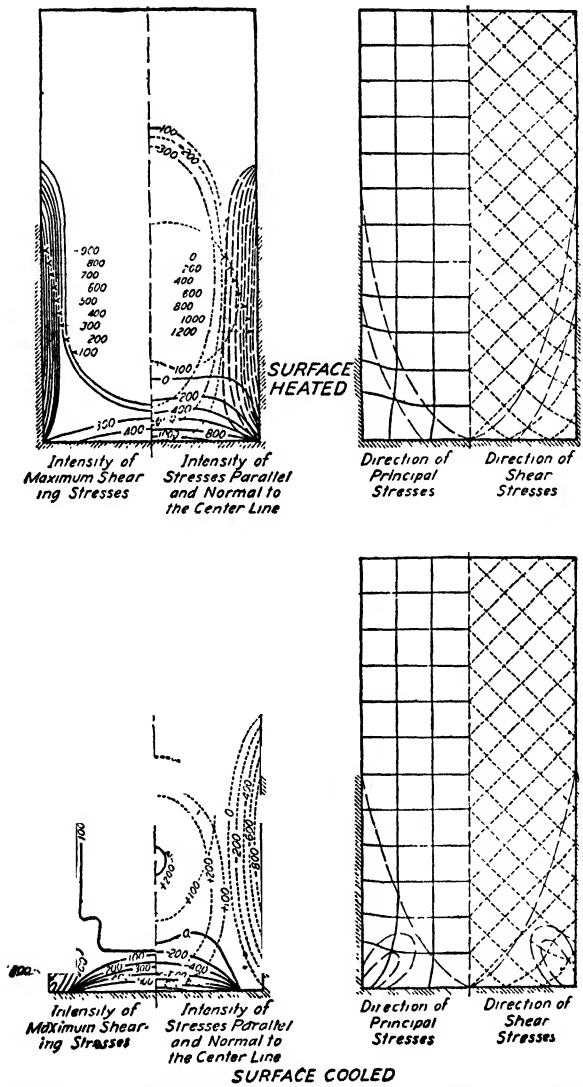


FIG. 249. Stresses in a brick heated on one end and one-third of the distance up the side. (*J. Am. Ceram. Soc.*)

(about 1650°F) for the first condition and were placed in still air to cool. Under the second condition, the objects were heated by placing suddenly in a furnace that had a temperature of 900°C (about 1650°F).

Spheres. Let us first consider the sphere that was suddenly cooled (Fig. 251). It will be noted that in general, the fractures follow great circles. When the portions of the sphere were separated, it was noted that

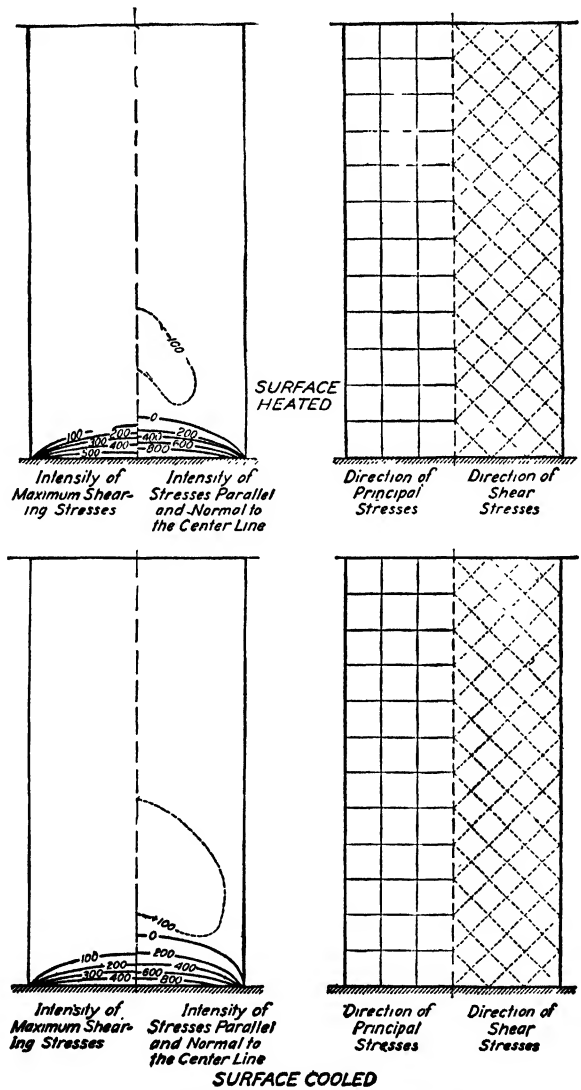


FIG. 250. Stresses in a wall. (*J. Am. Ceram. Soc.*)

the cracks entered the surface in every case at approximately 90 deg. On the other hand, when the sphere is suddenly heated, a quite different type of fracture is obtained, as shown in Fig. 252. In this case, the fractures entered the surface at 45 deg and tended to split off circular segments of the sphere having a height of approximately one-quarter the diameter.

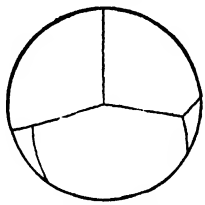


FIG. 251. Cracks in a sphere suddenly cooled. (*J. Am. Ceram. Soc.*)

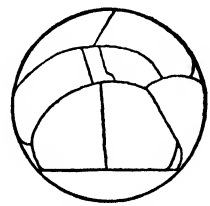


FIG. 252. Cracks in a sphere suddenly heated. (*J. Am. Ceram. Soc.*)

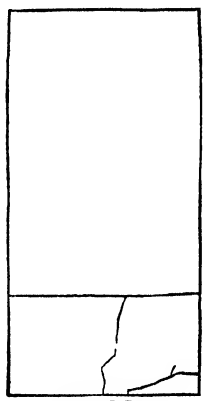


FIG. 253. Cracks in a brick suddenly cooled. (*J. Am. Ceram. Soc.*)

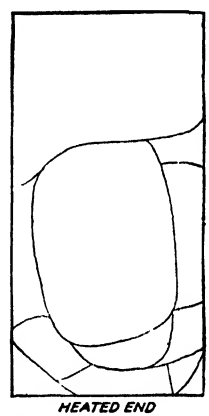


FIG. 254. Cracks in a brick suddenly heated. (*J. Am. Ceram. Soc.*)

Bricks. Standard-size bricks were made up of the same material as the spheres. They were also heated and cooled in the same way. In Fig. 253 are shown the fractures resulting from rapid cooling. It will be noted that the fractures enter, in nearly every case, at right angles to the surface and tend to break the brick into cubes. Figure 254 shows the same brick when heated suddenly. The typical spalling failure is shown at the edges and corners; and in every case, cracks enter the surface at approximately 45 deg.

As a brick does not consist of a homogeneous material, it is possible to have a weakening or disintegration of the structure aside from actual fractures. This effect is usually due to a difference between the coefficient of

thermal expansion of the bond and that of the grog particles. This may be due to the use of different materials for the grog and bond or to a low-burned bond when the material is the same throughout. Goodrich[19] has examined the loss in strength due to repeated heatings and finds a distinct weakening of the brick structure.

Conclusions. We may conclude from the preceding studies that spalling is due to both shear and tension failures. On sudden heating, spalling is due almost entirely to shear stresses and, on sudden cooling, to tension stresses except at the corners and edges, where shear stresses may still cause failure. The shear values are about equal on heating and cooling, but there are no large tension stresses on rapid heating.

Shear failure occurs suddenly; *i.e.*, complete pieces are split off at each cycle of heating, and they begin to split at the edges and corners, so that a brick tends to approach a spherical shape on the end. The shear cracks follow in the lines of shear determined by the photoelastic method very closely, as is indicated by the slight curvature of the shear fractures at the corners.

Tension cracks seldom occur near the corners but usually first appear halfway up the brick where the tensile stresses are a maximum. The tension cracks enter the surface at 90 deg. They do not occur as suddenly as do shear fractures but penetrate deeper and deeper at each cycle until finally the cracks meet at the center. In every case, the tension failures follow approximately the lines of principal stress, although the deviation was considerably more than for the shear stress, owing undoubtedly to the length of the cracks and the greater influence of discontinuities.

It should be noted at this time that the stress distribution is much altered after a crack starts, as was pointed out by Preston.[15] Generally, however, the tension cracks enter and leave at 90 deg and shear cracks at 45 deg to the surface. The fracture need not follow the direction of stress everywhere but will travel in such a way as to release the maximum strain energy. A great deal of confusion has been caused in the past by failure to differentiate between the effects of heating and cooling.

4. Theory of Spalling Due to Shear Stresses. As shown in the preceding pages, a spalling failure may occur either by a shear or by a tension fracture. If we first assume a shear failure, which appears to be the most common type, it is possible to analyze the mechanism of spalling in terms of the physical properties of the material.

Temperature Distribution. It is necessary at first to consider the distribution of temperature in a homogeneous solid. We shall first make the assumption that this solid has one infinite plane surface. Originally this solid is at a uniform temperature of t_0, but at time τ_0 the surface is suddenly cooled to a temperature of t_2. The problem is to find the temperature

distribution in the solid for different values of τ. For the solution, it will be necessary to apply Fourier's equation of heat flow. As the surface is infinite, the isothermal planes will be everywhere parallel to the surface of the solid. Putting $t_0 = t_1 - t_2$ or simply shifting the temperature scale, the temperature t at any distance below the surface x and at any time τ will be given by

$$t = \frac{2t_0}{\sqrt{\pi}} \int_0^{x/2h\sqrt{\tau}} e^{-\beta^2} d\beta \tag{1}$$

where h = a constant of the material.

The diffusivity of a material, or the rate at which a point in a hot body will cool under definite surface conditions, is known as h^2 and is equivalent

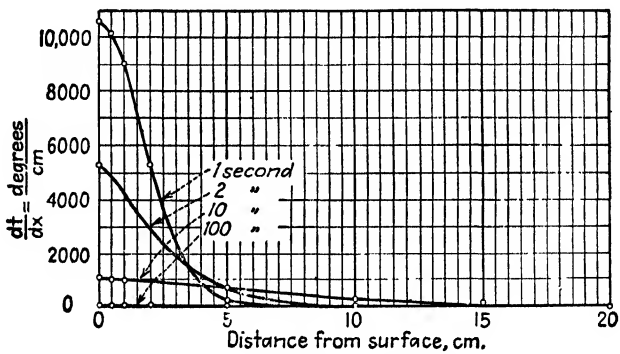


FIG. 255. Temperature gradients at different levels below the surface of a cooling body. (*J. Am. Ceram. Soc.*)

to $k/\rho c_p$, where k is the conductivity, ρ the density, and c_p the specific heat. It should be noted that the preceding equation is in the form of the probability integral and can therefore be readily evaluated from tables.

As will be shown later, the stress set up in a homogeneous material as a result of a change in temperature is proportional to the temperature gradient at any point. It will therefore be necessary to differentiate the preceding equation with respect to x.

We have

$$\frac{\partial t}{\partial x} = \frac{2t_0}{\sqrt{\pi}} e^{-x^2/4h^2\tau} \cdot \frac{1}{(-2h\sqrt{\tau})}$$

$$\frac{-t_0}{h\sqrt{\pi\tau}} e^{-x^2/4h^2\tau} = \frac{dt}{dx} \tag{2}$$

To show the practical application of this equation, curves have been plotted in Fig. 255 to give the temperature gradient $h = 0.080$ when a body is cooled suddenly from 850°C (about 1560°F) to room temperature.

The gradient is, of course, highest at the surface but falls rapidly toward the interior. Near the surface, the gradient falls rapidly with increasing time; but at a certain depth, the gradient increases with the time. This is one of the reasons why spalling does not usually take place immediately after the specimen is chilled.

In an actual case, the surface is not instantaneously cooled (1) because a cooling medium cannot be instantaneously introduced and (2) because perfect thermal contact cannot be made between the cooling medium and the surface of the brick. The equations can be modified to take care of this effect, as suggested by Ingersoll and Zobel,[2] by adding a fictitious distance beyond the true surface. In this instance, however, as we are not interested in the region very close to the surface, it will be more convenient to use a constant k to modify h.

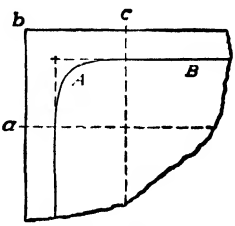


FIG. 256. The rounding of isothermal planes at the edge of a solid. (*J. Amer. Ceram. Soc.*)

Only the case of an infinite plane surface has been considered. At the edge of a solid, the isothermal planes will not be parallel to the surface but will be rounded off as in Fig. 256. This can be explained by considering that point A is cooled by the area abc in addition to the cooling received from an infinite surface such as a point at B. As the isothermals recede further from the surface, the area abc increases and corresponding departures from parallel conditions exist at corners.

It is important to notice that the temperature gradient is slightly less at the edges and the corners than at the faces of a cooling brick; hence, corners spall off because of mechanical weakness rather than because of greater temperature gradients.

Temperature Stresses. Now that we have the temperature distribution in a solid, it is possible to study the distribution of stresses. We shall first assume that the material is an elastic, homogeneous medium. It will be shown later that in the temperature range at which spalling occurs, the brick is perfectly elastic. The homogeneity will depend upon the structure of the brick and upon the process of manufacture.

The exact evaluation of the stresses in a brick under a given temperature distribution cannot be solved mathematically except in a few simple cases; however, it is required to find the tendency to spall only in terms of the physical properties of the material; *i.e.*, comparative but quantitative results are desired among various types of brick tested in the same manner.

Let us consider an isothermal plane ab in a portion of a heating or cooling brick at a given instant of time (Fig. 257). Let the temperature of the plane ab be t and that of another isothermal plane dx distant be $t + dt$, which gives the temperature gradient dt/dx. Let the plane cd cut the isothermal surfaces at a neutral point of shear. Now measure along ab a

distance s, and erect the plane ef. If the temperature throughout the brick were t, this plane would be normal to ab; but under the existing conditions, it will cut the $t + dt$ isothermal at a distance $s + s\alpha\, dt$ from *cd.* The coefficient of expansion is α.

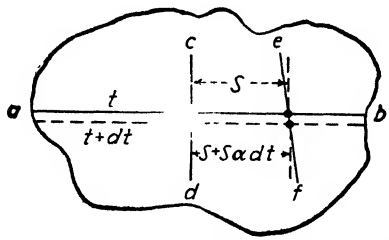


FIG. 257. A portion of a heating or cooling brick. (*J. Am. Ceram. Soc.*)

The shear strain is measured by the deflection of one plane with respect to another divided by the distance between them. In this case,

$$\phi = \frac{s\alpha\, dt}{dx} = s\alpha \frac{dt}{dx} \tag{3}$$

This means that the strain set up in a heating or cooling body is proportional to the size, the coefficient of thermal expansion, and the temperature gradient. This explains why large glassware cracks on cooling or heating more readily than small ware. In large pieces of refractory ware, the temperature distribution may be so uneven that strict proportionality to s may well be doubted. This does not greatly concern us, for we shall compare specimens of the same shape and size and with the same temperature gradient. The shear fracture theoretically should occur at 45 deg to the isothermal but often is parallel to it. However, the direction of fracture does not affect the reasoning. As pointed out by Clark,[51] the maximum stress or strain is not strictly a constant of the material at a given temperature but varies to some extent with the duration of stress.

From Eq. (2)

$$\frac{dt}{dx} = \frac{k_1}{h} \tag{4}$$

where k_1 = a constant

This follows, for dt/dx is closely proportional to $1/h$ because small changes of h in the term $e^{-x^2/4h^2\tau}$ have little effect when τ is reasonably large.

Then the tendency to spall S_s is

$$\frac{\phi}{\phi_b} = \frac{s\alpha\,(dt/dx)}{\phi_b} = \frac{s\alpha\,(k_1/h)}{\phi_b} = k_1 \frac{s\alpha}{h\phi_b} = k_2 \frac{\alpha}{h\phi_b} \tag{5}$$

where ϕ_b = the maximum shearing strain or flexibility

This shows that the spalling tendency of a brick is proportional to the

coefficient of thermal expansion divided by the square root of the diffusivity and maximum shearing strain.

5. Theory of Spalling Due to Tensile Stresses. The preceding theory has been based entirely on the shear failure of a material under shear stresses. It was seen that this failure would occur on sudden heating of the brick. The sudden heating produces local compressive stresses in the material, since the portion at a higher temperature tends to try to expand, but this being prevented by the cooler portions places the hotter portion of the brick in compression. It is known that brittle materials fail in shear when subjected to compressive stresses; hence, we get a shear failure under these conditions.

If the brick is suddenly cooled, a different phenomenon is involved. When one portion of the brick is suddenly cooled below the temperature of the adjacent material, the part of the brick at the lower temperature tends to contract, but this contraction is prevented by the adjacent portions, which are at a higher temperature. In this case, tensile stresses are set up in the cooler portion; and since the shearing strength of a brittle material is usually considerably greater than the tensile strength, the brick will fail in tension, provided sufficiently rapid local cooling is present.

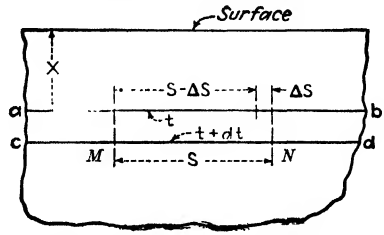


FIG. 258. Illustration of tensile stresses in a heating or cooling brick.

Let us then visualize a portion of the brick as shown in Fig. 258, which we will assume to be at the uniform temperature t_0. This means that at the start, the isothermal planes *ab* and *cd*, which are initially separated by the distance dx, are at the same temperature t_0. The surface of the brick is now cooled to a temperature t_2; and at a later time τ, the planes *ab* and *cd* possess temperatures t and $t + dt$, respectively, where the temperature is given by Eq. (1). Let us consider a gage length s between points M and N on plane *cd*. As a result of the lower temperature on plane *ab*, the material on this plane tends to contract by an amount ΔS. This contraction is, however, prevented by the adjacent material, and a tensile strain is set up in plane *ab* of amount

$$\Sigma = \frac{\Delta S}{S} = \alpha \cdot dt \tag{6}$$

where α = the coefficient of thermal expansion

Now, from Eq. (4)

$$\frac{dt}{dx} = \frac{k_1}{h}$$

and

$$\sigma = E \cdot \Sigma \tag{7}$$

It follows from the preceding equations, then, that

$$\sigma = E \cdot \alpha \cdot dt = E \cdot \alpha \cdot \frac{k_1}{h} \cdot dx \tag{8}$$

If σ_b is the breaking stress of the material or the so-called "tensile strength,"

$$\sigma_b = E \cdot \Sigma_b \tag{9}$$

where Σ_b = the tensile breaking strain

The tendency to spall then becomes

$$S_t = \frac{\sigma}{\sigma_b} = \frac{E \cdot \alpha \cdot k_1 \cdot dx}{Eh\Sigma_b} = k_1 \cdot dx \frac{\alpha}{h\Sigma_b} \tag{10}$$

It will be noted that Eq. (10) has the same units and is in the same form as Eq. (5) of the preceding section. Instead of the shear strain σ_b at fracture, we have the tensile strain Σ_b; and in place of the distance S from the neutral place of shear, we have the distance dx over which the temperature drop dt exists.

Let us now compare this equation temperature with the Winkelmann-Schott[1] equation, which is as follows:

$$\sigma = -\frac{A'A''}{A} \frac{t_0 \cdot E \cdot \alpha x}{2h\sqrt{\tau}} \tag{11}$$

where A', A'', A = constants

t_0 = the temperature of the outer layer

The tendency to spall is

$$S_t' = \frac{\sigma}{\sigma_b} = -\frac{A' \cdot A'' \cdot t_0 \cdot \alpha \cdot x}{2Ah\sqrt{\tau}\,(\sigma_b/E)} \tag{12}$$

or

$$S_t = k_3 \cdot x \cdot \left(\frac{\alpha}{h\Sigma_b}\right) \tag{13}$$

where

$$k_3 = -\frac{A'A''t_0}{2A\sqrt{\tau}} \tag{14}$$

It is thus seen that the Winkelmann-Schott equation can be put in the same form as given by Eq. (5) or (10). In the derivation given in the original article by Winkelmann and Schott, the size factor x was absorbed in another constant B, where B is essentially Kx. This, of course, can be done, since the purpose was to compare the spalling properties of various glasses for the same values of τ and x.

6. Experimental Confirmation of Theory. In order to determine the validity of the equation for tendency to spall, the physical characteristics of a number of different bricks shown in Table 78 were tested and the tendency to spall, as computed from the preceding formula, was compared with the actual spalling characteristics of the brick in Table 79.

TABLE 78. CHARACTERISTICS OF BRICK TESTED FOR SPALLING

Material	Grog	Bond	Hardness	Approximate burning temperature		Remarks
				°C	°F	
A. Fireclay.....	Very coarse	Soft	Soft	1200	2300	Commercial brick
B. Sillimanite.....	Medium	Little	Hard	1680	3050	Special brick
C. Fireclay.....	Very coarse	Soft	Medium	1430	2600	Same as A (hard burn)
D. SiC.....	20-mesh	Molasses	Hard	1540	2800	Special brick
E. Fireclay.....	Coarse	Soft	Soft	1316	2400	Commercial brick
F. Bauxite.....	Fine	Little	Hard	1704	3100	Special brick
G. Fireclay.....	Medium	Soft	Soft	1316	2400	Commercial brick
H. Kaolin.....	Medium	Little hard	Very hard	1650	3000	Commercial brick
I. Fireclay.....	Fine	Soft	Soft	1200	2300	Commercial brick
J. Fireclay.....	Medium	Hard	Hard	1200	2300	Commercial brick
K. Fireclay.....	Fine	Soft	Soft	1200	2300	Commercial brick
L. Spinel.....	Medium	Hard	Hard	1370	2500	Commercial brick
M. Silica.....	Fine	None	Hard	1480	2700	Commercial brick
N. Same as C preheated to 2900°F						

Flexibility in Shear. In order to measure the characteristics of the bricks as listed above, a number of 1 × 1 × 9-in. bars were sawed out of each specimen. These bars were then cemented into holders, and the angle and torque measured up to the breaking point at a temperature of 500°C (about 930°F).

Such a low temperature is justified because it has been noticed that spalling nearly always occurs at about red heat. In all cases where the specimen was carefully held, there was no permanent set after removing the torque until a point was reached just before failure; *i.e.*, the specimens all acted as if perfectly elastic. The bricks tested are described in the table above and represent a wide range. Some are experimental bricks; others are of extensively used commercial brands.

The Coefficient of Expansion. The coefficient of thermal expansion of each type of brick was measured at 500°C (about 930°F). In general, the brick having the greatest coefficient of thermal expansion had the highest

TABLE 79. CONSTANTS FOR THE BRICKS TESTED

Brand	ϕ_b	α	h	$(\alpha/\phi_b h)$	Number of quenches
A.....	0.114	0 0000051	6.2	72×10^{-7}	26.5
B.....	0.052	0.0000039	6.5	115	8.0
B.....	0.052	0.0000039	6.5	115	24.0
C.....	0.050	0.0000050	6.3	157	23.0
D.....	0.072	0.0000031	9.9	44	*
E.	0.057	0.0000053	6.5	143	15.6
F.....	0.032	0.0000037	6.2	110	2.0
F.....	0.032	0.0000037	6.2	110	15.0
G...	0.090	0.0000104	6.2	187	12 2
H.....	0.050	0.0000063	6.4	197	10 6
I.....	0.107	0.0000133	6.3	197	8.4
J.....	0.050	0.0000071	6.0	237	5 2
K..... .	0.089	0.0000126	6.2	229	2.7
L..... ...	0.032	0.0000116	6.4	567	2.4
M	0.094	0.0000405	6 7	644	0.3
N.....	0.060	0.0000072	6.1	197	

* No exactly comparable spalling value was available for this brick; but it is undoubtedly lower than should be expected, as an oxidizing atmosphere tends to convert the SiC into SiO_2 and thereby to raise the coefficient of thermal expansion.

content of silica, but we are by no means justified in using the silica content of a brick as an index of its coefficient.

Diffusivity. The value of the diffusivity can, of course, be obtained by measurements of thermal conductivity and specific heat. These measurements, however, are laborious and slow, so a simple method of measuring the relative diffusivity was devised. A 2-in. cube of the material was cemented from four 1 × 1 × 2-in. blocks with a thermal junction at the center, was suspended by the junction wires in an electric furnace until it had reached a constant temperature of about 550°C (about 1020°F), and then was taken out and suspended in a room free from drafts. The temperature of the center was recorded, and the slope of the cooling curve at 500°C (about 930°F) taken as the value for the diffusivity. This method is rapid and accurate where only relative values are desired.

The values of the diffusivity given are entirely arbitrary, and the results are comparable only among themselves, but it will be noted that with the exception of the silicon carbide specimen, the values of h vary only a few per cent and cannot be an important factor in spalling.

Comparison with Actual Spalling Tests. The results from laboratory air-spalling tests are also given. A comparison between this test and actual service results has been made, and the agreement is generally good. From five to ten bricks of each kind were spalled, and the average taken.

Attention should be called to the two values given for bricks *B* and *F*. These two bricks showed the common type of shear spalling at the corners for several quenches, then suddenly broke across the center with a tension failure. The first value in the table gives the quenches actually obtained, and the second is estimated from the amount lost by shear. The first values have been disregarded in drawing the curves.

If the value of $\alpha/h\phi_b$ is an index of the spalling tendency of a brick as indicated by the theory, then these values plotted against the number of quenches for each specimen should fall along a curve rather than be widely

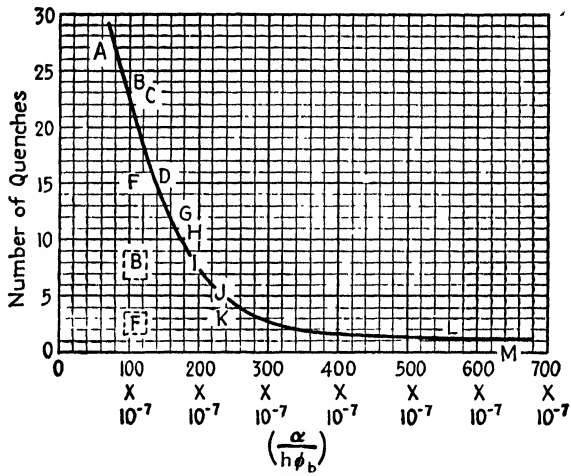


FIG. 259. A plot showing correlation between theoretical and experimental values of spalling. (*J. Amer. Ceram. Soc.*)

scattered. Such a plot has been made in Fig. 259, and it is quite clear that the points group themselves into a definite band. The deviations that occur can be explained by the fact that some of the bricks were altered from their original characteristics in heating.

Specimen *K*, which is considerably below the mean curve, was noticeably laminated in structure. The higher values for bricks *B* and *F* were only estimates.

The form of the curve is of interest, for it approaches a rectangular hyperbola asymptotic to the two axes. When the value of $\alpha/\phi_b h$ is high, the bricks show little difference in spalling resistance, as they are almost completely shattered at the first temperature change. On the other hand, the bricks having a low value of $\alpha/\phi_b h$ increase rapidly in spalling resistance as $\alpha/\phi_b h$ is decreased. This behavior is not unexpected, as it is simply an approach to a classification of bricks into two sets: those which spall on the first quench and those which do not spall under an infinite number of quenches.

The best spalling brick of those tested withstood 26 quenches and had a value for $\alpha/\phi_b h$ of 72×10^{-7}. Suppose that by slightly increasing the flexibility or by decreasing the coefficient of thermal expansion, a value of 50×10^{-7} were obtained; the brick should then withstand about 50 quenches. This illustrates the possibilities of making remarkable non-spalling brick.

On the whole, it would seem that the theoretical work agrees with practice as closely as the nature of the tests allows. Although this method cannot be recommended to replace the usual spalling tests without a more thorough trial, it is felt that more information is obtained by it as to the causes of spalling in a certain brick than by other methods.

It is interesting to note that Booze[11] and Phelps[16] independently came to the same conclusions after testing a number of experimental bricks for coefficient of thermal expansion, diffusivity, and flexibility. They found that the best spalling bricks had the greatest flexibility and that the diffusivity had no appreciable effect. Endell's[26] work on magnesite brick checks this theory.

7. Laboratory Spalling Test. The expense and the time required to determine the spalling characteristics of bricks in service are so great that a laboratory spalling test is highly desirable.

A number of spalling tests have been suggested and used. In most cases, they consist in subjecting the brick to a severe thermal shock in order that the test may produce definite results in a reasonably short time. Tests on single bricks as formerly used have now been almost abandoned, as they do not in all cases correspond to service conditions. Therefore the present ASTM test on a panel will be described. It is quite satisfactory but requires expensive equipment.

PANEL TEST FOR RESISTANCE TO THERMAL AND STRUCTURAL SPALLINGS OF REFRACTORY BRICK

ASTM Designation: C 38-42[1]

ADOPTED, 1936; REVISED, 1942, 1945, 1947

This standard of the American Society for Testing Materials is issued under the fixed designation C 38; the final number indicates the year of adoption as standard or, in the case of revision, the year of last revision.

1. Scope. This method of test is intended to show the resistance of refractory brick to the separate and combined effects of structural and thermal spalling. The test is believed to give a sufficient simulation of service conditions to suggest

[1] ASTM Standards are subject to revision. The Society's headquarters, in Philadelphia, may be consulted for the latest information. Only minor changes from the 1942 revision given here have been made in the 1947 revision.

its use as a suitability test for certain classes of service that have been correlated with the test data (see NOTE).

NOTE: Such correlation is now available in the case of high-heat-duty clay brick for stationary boilers, malleable iron furnace bungs, and incinerator furnaces.

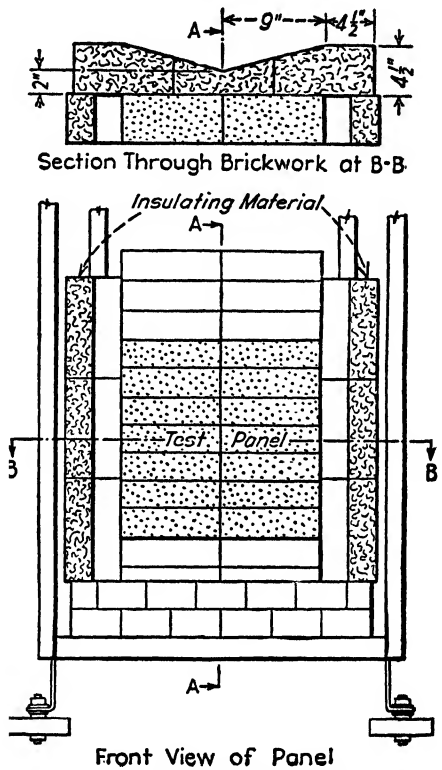


FIG. 260. Panel frame and brickwork. The brick around the test panel are dummy brick which are used to help maintain uniform conditions within the panel.

2. Apparatus. The following apparatus and equipment[1] are needed:

a. Panel Frame. A panel framework shall be used which is essentially the same as that shown in Fig. 260.

b. Preheating Furnace. A preheating furnace shall be used, constructed essentially like the design shown in Fig. 261.

c. Spalling Furnace. A spalling furnace shall be used, constructed in a manner as shown in Fig. 262.

[1] The complete set of drawings necessary for the construction of the panel spalling equipment would require too much space to be included with the procedure, but these are available at a nominal charge from the Refractories Fellowship, Mellon Institute of Industrial Research, Pittsburgh, Pa.

d. Temperature-measuring Instruments. The temperature of the test panel during the preheating shall be measured by means of an optical pyrometer. The spalling furnace temperature shall be determined by means of a platinum, platinum-rhodium thermocouple.

e. Air Supply. Means shall be provided for delivering air through each cooling unit at a specified rate.

f. Transfer Facilities. A suitable means, such as a track or trolley, shall be provided for transferring the test panels.

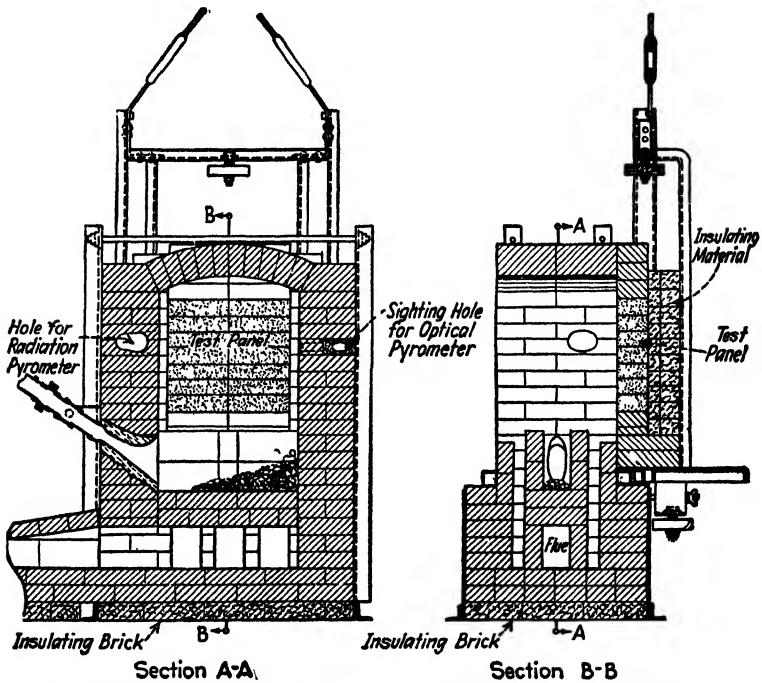


FIG. 261. Design of preheating furnace. In section *BB* there is shown in position one of the two panels used during the preheating.

3. Test Specimen. Whenever possible, the panel test specimen shall consist of 9-in. straight brick. When shapes of other sizes are to be tested, these shall be cut so as to be not more than 3 in. in thickness by 9 in. in length by 4½ in. in width.

4. Panel Construction. The test brick shall be laid up so as to form a panel not less than 18 in. square, so that a 9- by 2½-in. surface of each brick will be exposed to the heat-treatment. Each test brick shall be labeled with ceramic paint on the face opposite that to be tested and then weighed to the nearest 0.05 lb. There shall be placed about the panel test specimen a suitable grade of refractory dummy brick, in the manner shown in Fig. 260. The dummy brick shall extend ½ in. beyond the surface of the test panel. All brick in the test panel shall be

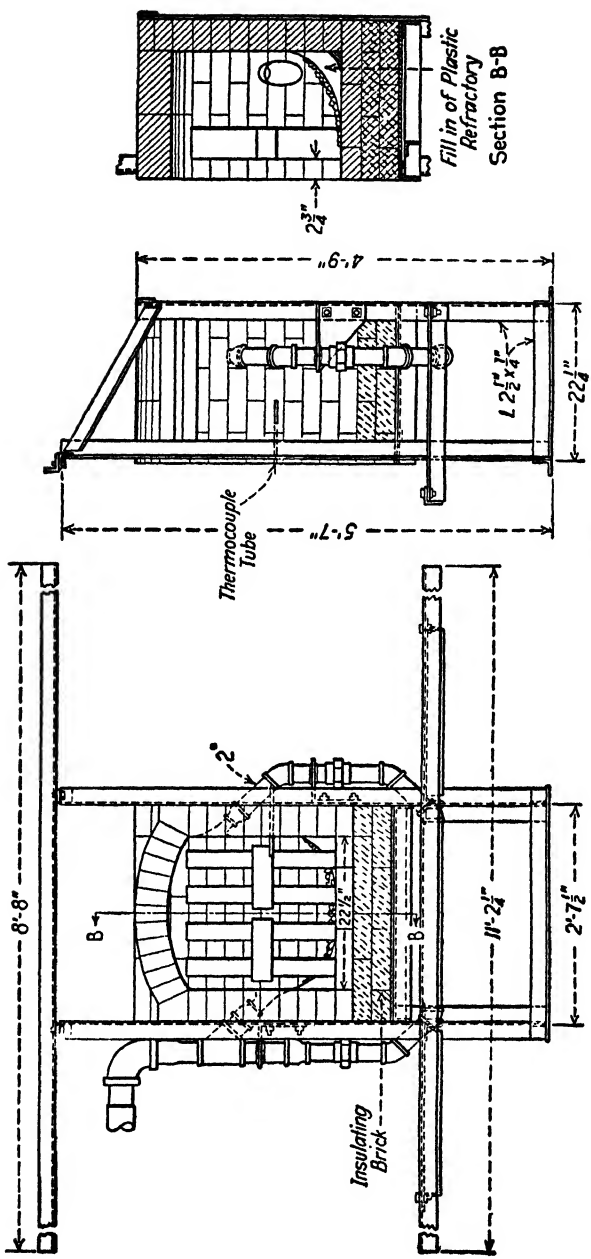


FIG. 262. Furnace of the spalling equipment.

laid up with refractory kaolin unless otherwise specified. The joints shall not be thicker than $\frac{1}{16}$ in. The insulation shall consist of a material suitable for service at 1300°C and of a specified insulating value.

5. Preheating Test Panels. The prepared test panels shall be placed in position on either side of the preheating furnace. When only one lot of brick is to be tested, a dummy panel should be used. The joint between the ends of the panel dummy brick and the preheating furnace shall be sealed with plastic kaolin. During the heating of the panels, the surface of the test brick opposite that being heated shall be insulated in the specified manner so as to maintain a suitable temperature gradient in the test brick. The furnace is to be operated so that the temperature specified for preheating shall be reached in not less than 5 hr nor more than 8 hr and maintained 24 hr. The permissible variation in temperature may be ±20°F or ±10°C, but the average of the temperature during the run shall be that specified. After completing the preheating, the test panel shall be left in position for not less than 8 hr before being removed. As a result of this heat-treatment, any tendency toward fusion, vitrification, swelling, or shrinkage will be evident and any development of structural spalling will be apparent. A record shall be made of the condition of the brick, indicating the extent of the fusion, vitrification, swelling, or shrinkage. If shrinkage takes place, a record shall be made of its nature, *i.e.*, whether this occurs as a shrinkage of each brick as a unit or as the development of cracks on the surface of each brick. The surface of the test panels may be photographed.

6. Spalling. The panels shall then be subjected to thermal spalling by heating them in a specified time to a specified temperature and rapidly cooling by means of a prescribed blast. The panels shall be placed in position in front of the spalling furnace in the manner shown in Fig. 262. The temperature of the spalling furnace shall be raised within 3 hr to the specified temperature. During the heating period, the panels shall be alternately placed in position in front of the furnace so that each may be heated to about the same temperature. The position of the panels shall be changed at temperatures of 400, 200 and 100°C below the final furnace temperature. During this period, the panels shall not be cooled by means of the cooling blast. After the final temperature of spalling is obtained, the panels shall be held in position for a specified time and then shifted so as to expose the heated panel for cooling. After each panel has been subjected to the required number of cycles, the furnace shall be allowed to cool, but the cooling procedure for the panels shall be conducted so that each panel receives two additional periods.

7. Dismantling the Panels. When the panels have cooled sufficiently so that the brick can be handled, the test panel shall be carefully dismantled. The test brick shall be reweighed to the closest 0.05 lb, and the loss in weight recorded as percentage of the original weight.

8. Report. The report may include a photograph of the panel after preheating and shall include comments as to its condition. The average spalling loss for the whole panel shall be given, as well as a photograph of the spalled brick arranged in the manner shown in Fig. 263.

STANDARD METHOD OF PANEL TEST FOR RESISTANCE TO THERMAL AND STRUCTURAL SPALLING OF HIGH HEAT DUTY FIRECLAY BRICK

ASTM Designation: C 107-42[1]

ADOPTED, 1936; REVISED, 1940, 1942, 1945, 1947

This Standard of the American Society for Testing Materials is issued under the fixed designation C 107; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision.

FIG. 263. A typical panel after the spalling test. (*Courtesy of the American Refractories Institute.*)

1. Scope. This method of test covers the procedure for determining the resistance of fireclay brick used for stationary boilers, malleable-iron furnace bungs, and incinerator furnaces to the separate and combined effects of structural and thermal spalling. This method makes use of the general requirements and procedure prescribed in the Method of Panel Test for Resistance to Thermal and Structural Spalling of Refractory Brick (ASTM Designation C 38) of the American Society for Testing Materials and supplements that method by giving the detailed requirements of the procedure to be followed in testing refractories for use in stationary boilers, malleable-iron furnace bungs, and incinerator furnaces.

[1] ASTM Standards are subject to revision. The Society's headquarters, in Philadelphia, may be consulted for the latest information.

2. Apparatus and Test Specimens. The apparatus and test specimens shall be in general as described in the Method of Panel Test for Resistance to Thermal and Structural Spalling of Refractory Brick (ASTM Designation C 38) of the American Society for Testing Materials.

3. Procedure. The procedure shall be in general as outlined in the Method C 38, supplemented by the procedure for preheating and spalling as prescribed in the following Secs. 4 and 5.

4. Preheating Test Panels. *a.* The test brick shall be laid up with kaolin having a pyrometric cone equivalent not below cone No. 34.

b. The test panels and dummy brick shall be insulated with group 26 insulating firebrick weighing 46 ± 2 lb per cu ft.

c. The temperature of the panel faces shall be maintained so as to average 2910°F (1600°C) by means of a gas-fired furnace for a period of 24 hr.

d. The furnace gas pressure during the 24-hr preheating period shall be within the limits of 0.4 to 0.5 in. of water for gas-fired furnaces.

5. Spalling. *a.* The panel insulation shall be removed.

b. The gas-fired furnace shall be operated so as to obtain a temperature of 2550°F (1400°C) before the panels are cooled by means of the blast.

c. The period for heating shall be 10 min and for cooling 10 min making a 20-min cycle.

d. The cooling shall be accomplished by means of an air-water mist blast, which shall be delivered through a vertical manifold with an opening measuring 3½ by 24 in. as shown in the Method C 38. Air shall be delivered through each cooling unit at the rate of 1,400 cu ft per min. The water used in the four spray units shall be filtered and measured by means of a meter. The spray nozzles shall be regulated so as to deliver water at the rate of 2½ gal during the first 8 min of the cycle. No water shall be used during the last 2 min. The cooling units shall be operated with a reciprocating motion so as to pass back and forth across the surface of the entire panel, including the dummy guard brick, 125 times in 10 min.

e. The spalling treatment shall consist of 12 cycles, after which the furnace shall be shut off and the panels given 2 additional cooling cycles without the water mist.

f. After carefully dismantling the panel, the kaolin shall be scraped off with a trowel, removing such pieces of the brick that separate easily. No attempt shall be made to separate pieces that might be removed by prying or tapping.

STANDARD METHOD OF PANEL TEST FOR RESISTANCE TO THERMAL AND STRUCTURAL SPALLING OF SUPER DUTY FIRECLAY BRICK

ASTM Designation: C 122-42

ADOPTED, 1937; REVISED, 1940, 1942, 1945, 1947

This Standard of the American Society for Testing Materials is issued under the fixed designation C 122; the final number indicates the year of original adoption as standard or, in the case of revision, the year of last revision.

1. Scope. This method of test covers the procedure for determining the resistance of super-duty fireclay brick to the separate and combined effects of structural and thermal spalling. This method makes use of the general requirements and procedure prescribed in the Method of Panel Test for Resistance to Thermal and Structural Spalling of Refractory Brick (ASTM Designation C 38) of the American Society for Testing Materials, and supplements that method by giving the detailed requirements of the procedure to be followed in testing super-duty fireclay brick.

2. Apparatus and Test Specimens. The apparatus and test specimens shall be in general as described in the Method of Panel Test for Resistance to Thermal and Structural Spalling of Refractory Brick (ASTM Designation C 38) of the American Society for Testing Materials.

3. Procedure. The procedure shall be in general as outlined in Method C 38, supplemented by the procedure for preheating and spalling as prescribed in the following Secs. 4 and 5.

4. Preheating Test Panels. *a.* The test brick shall be laid up with kaolin having a pyrometric cone equivalent not below cone No. 34.

b. The test panels and dummy brick shall be insulated with group 26 insulating fire brick weighing 46 ± 2 lb per cu ft.

c. The temperature of the panel faces shall be maintained so as to average 3000°F (1650°C) by means of a gas-fired furnace for a period of 24 hr.

d. The furnace gas pressure during the 24-hr preheating period shall be within the limits of 0.4 to 0.5 in. of water for gas-fired furnaces

5. Spalling. *a.* The panel insulation shall be removed.

b. The gas-fired furnace shall be operated so as to obtain a temperature of 2550°F (1400°C) before the panels are cooled by means of the blast.

c. The period for heating shall be 10 min and for cooling 10 min making a 20-min cycle.

d. The cooling shall be accomplished by means of an air-water mist blast, which shall be delivered through a vertical manifold with an opening measuring 3½ by 24 in. as shown in the Method C 38. Air shall be delivered through each cooling unit at the rate of 1,400 cu ft per min. The water used in the four spray units shall be filtered and measured by means of a meter. The spray nozzles shall be regulated so as to deliver water at the rate of 2½ gal during the first 8 min of the cycle. No water shall be used during the last 2 min. The cooling units shall be operated with a reciprocating motion so as to pass back and forth across the surface of the entire panel, including the dummy guard brick, 125 times in 10 min.

e. The spalling treatment shall consist of 12 cycles, after which the furnace shall be shut off and the panels given 2 additional cooling cycles without the water mist.

f After carefully dismantling the panel, the kaolin shall be scraped off with a trowel, removing such pieces of the brick that separate easily. No attempt shall be made to separate pieces that might be removed by prying or tapping.

In using the ASTM panel test for spalling, the following losses are generally used as limits.

Conditions	Average Weight Loss, Per Cent
Average spalling	15
Moderately severe	10
Severe (malleable furnace bungs)	5–7.5
Extremely severe (super duty class)	4

The ASTM panel spalling test equipment has been installed in a number of laboratories and, in spite of the considerable cost of operation and large floor space required, has been well worth while when reliable spalling results are required. This test is valuable to the producer of refractories for a control test of his product and for the development of improved refractories. It also is of aid to the consumer in assuring that the standard of quality of the refractories purchased is adhered to. Those who do not have enough testing to justify the cost of this equipment may have their product tested at a commercial testing laboratory.

The U.S. Navy simulative service furnace, as described in Chap. XVII, can be used for a spalling test with results agreeing well with those obtained in service.

8. Spalling Characteristics of Various Bricks. In Table 80 are given the spalling resistance of a number of fireclay brick as measured by the ASTM panel spalling test.

Silica brick are not at all resistant to spalling in the low-temperature range; but once they are above the inversion temperature, they are very resistant to wide changes in temperature because of the flatness of the expansion curve in this region. This is the reason that they give such good service in regenerative furnaces.

Chrome and magnesite brick, because of their rather high coefficient of thermal expansion, are not so resistant to spalling as fireclay brick, but great improvements have been made in the last few years in providing a more flexible structure[26] and thus increased resistance.

Silicon carbide brick have an excellent resistance to spalling.

9. Effect of the Brick Structure on Spalling. The structure of the brick and the method of manufacture have a considerable influence on spalling. Data given below illustrate the effect of various factors. These data are for one particular clay and will not be exactly the same for others, but the trend should be general.

Effect of Grog Size. A number of bricks were made up with various sizes of grog, other conditions being the same. The spalling resistance for each grog size is given in Table 81. The spalling resistance increases

TABLE 80. SPALLING RESISTANCE OF FIRECLAY BRICK BY THE ASTM PANEL SPALLING TEST*
(Courtesy of the American Refractories Institute)

Method of manufacture	Brand No.	Loss in panel spalling test, per cent	Porosity, per cent
Hand-made	A	12.8	17.8
	B	8.0	25.0
	C	6.3	24.0
	D	21.0	22.4
Stiff-mud	E	25.0	15.7
	F	28.0	13.7
	G	20.5	20.1
	H	2.5	24.4
	I	0.5	30.0
Dry-press	J	14.8	20 9
	K	5.5	16 7
	L	13.0	17.5
	M	2.0	23.0
	N	1.0	14.0

* These panels were preheated 1600°C according to specifications C-107.

steadily with the grog size for a given burning temperature. These results were obtained on single bricks, and somewhat different values might be obtained by panel spalling methods.

TABLE 81. EFFECT OF GROG SIZE ON SPALLING RESISTANCE

Burned at	1649°C. (3000°F.)	1677°C. (3051°F.)	1704°C. (3099°F.)
2 mesh	20 cycles	12 cycles	5 cycles
3½ mesh	11 cycles	6 cycles	3 cycles
4 mesh	6 cycles	3 cycles	1 cycle
20 mesh	1 cycle	1 cycle	1 cycle

Effect of Amount of Grog. In Fig. 264 is plotted a curve of spalling resistance against percentage of grog. It is interesting to note that the maximum spalling resistance occurs at 40 per cent of bond, or at the condition where the pores are just filled up. Above or below this point, the spalling resistance falls off rapidly, probably owing to loss of flexibility.

Effect of Burning Temperature. Figure 265 shows a curve of spalling resistance plotted against burning temperature. There is a minimum value at 1620°C (about 2950°F) and a maximum at 1650°C (about 3000°F). This type of curve has been observed a number of times for this particular

brick, but it may not apply to all others. The minimum point is probably due to the decreasing flexibility of the structure with increased temperature. Beyond 1600°C (about 2950°F), the free silica is dissolved and the coefficient of thermal expansion is lowered, which increases the spalling resistance up to 1635°C (about 3000°F). After this, the structure gets

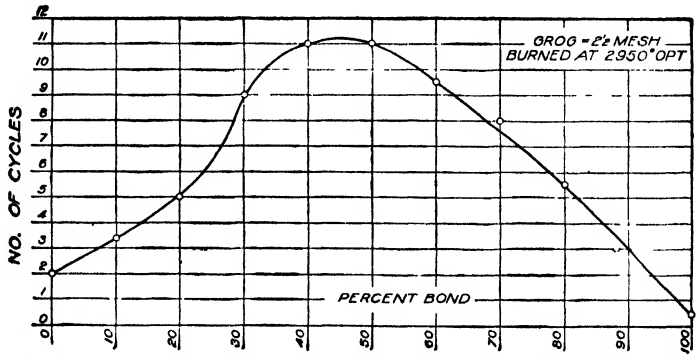


FIG. 264. The influence of the amount of bond on spalling resistance.

more rigid and the spalling resistance falls off. In general, it may be said that increasing the burning temperature decreases the resistance to spalling. This is shown in Table 82, where the spalling resistance is given for a number of bricks before and after preheating. Again it is probable that the hard-burned bricks would have shown up comparatively better if the spalling had been made with the panel test or in service.

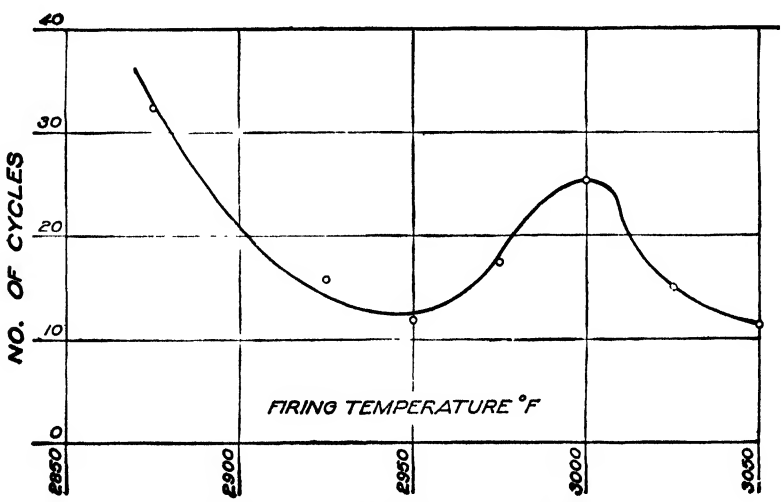


FIG. 265. Influence of burning temperature on spalling resistance.

Characteristics of a Good Spall-resisting Brick. We usually have a specified material from which to make a brick. With this material, it is impossible to alter the diffusivity appreciably, and only small changes can be made in the coefficient of thermal expansion. Therefore, if we desire to make the best spall-resistant brick from a given material, we must do two things: (1) make a structure having the greatest possible flexibility and (2) eliminate all possible flaws and laminations.

TABLE 82. EFFECT OF PREHEATING ON SPALLING RESISTANCE

Brick	As burned, cycles	Preheated to 1670°C (3038°F) cycles
Missouri	45	4
Missouri (diaspore)	29	13
Pennsylvania	12	1
	18	4
	15	1
	22	2
	11	1
	4	1
Kaolin	12	12

Flexibility can best be obtained by using a large size of grog, a high degree of porosity, and a low degree of vitrification. These characteristics cannot be obtained to a high degree without sacrificing others of considerable importance. For example, bricks could easily be made to withstand 50 cycles in the air-spalling test; yet they would be mechanically weak and would probably have a high residual shrinkage. It has often been noticed that when a series of bricks are tested for spalling, there will be a great variation between the best and the worst out of the same lot. Where it is known that these bricks were made by identically the same process and that they all were burned at the same temperature, we can conclude only that the difference in spalling resistance is due to some lack of homogeneity in the structure of the brick. It is impossible to state definitely that any one method of making bricks gives the best or the worst spalling results, although it is generally found that re-pressed bricks, when properly tempered, give greater uniformity in the spalling test. We are greatly in need of a simple test to determine which bricks in a given lot will give a poor resistance to spalling. Some investigations have been made to test each brick by noting the sound emitted when struck with a hammer; but as yet, no very definite results have been obtained along this line. The recent work of Ford and Rees[53] on magnesite bricks is very valuable in correlating structure and spalling resistance.

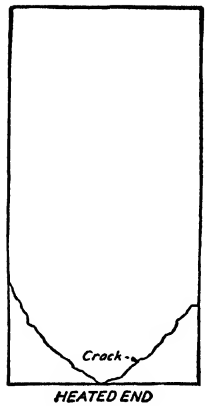
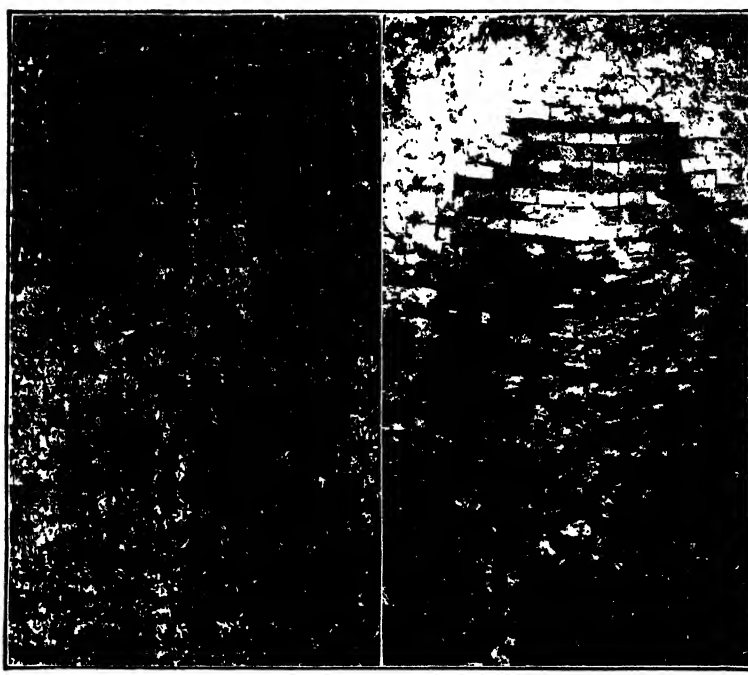


FIG. 266. A type of spalling fracture often occurring in service. (*J. Am. Ceram. Soc.*)

FIG. 267. Tension crack in end of a brick due to spalling. (*J. Am. Ceram. Soc.*)



FIGS. 268 and 269. Boiler furnace wall showing spalling under oil-fired conditions. (*Stone and Webster Company.*)

10. Spalling Fractures in Service. The types of spalling fracture in service walls are quite varied. Perhaps the most typical is that shown in Fig. 266, which consists of two shear cracks coming together at the center of the brick. There is often a small tension crack in the end of the brick, as shown in Fig. 267. The fracture corresponds well with the determined stresses for this condition. This type of failure is not often serious, because the fragments are so large that they stay in place. In other cases, the wall is pretty well shattered, as shown in Figs. 268 and 269.

Another type of spalling failure is the separation of a thin layer of material from the face of the brick, as shown in Fig. 270. This usually occurs with bricks of low vitrifying points or with slagged surfaces, and the fracture runs between the vitrified material and the body of the brick. Often layer after layer will peel off, giving a considerable length of service before the wall becomes too thin.

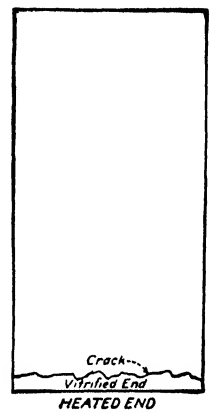


FIG. 270. Separation of a thin layer due to vitrification. (*J. Am. Ceram. Soc.*)

Exposed corners in a furnace are quite subject to spalling and should be avoided in design where possible. This type of failure by shear is shown in Fig. 271.

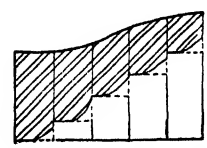


FIG. 271. Spalling of exposed corners of a furnace.

Spalling in a wall is greatly augmented by compression loads due to expansion. Expansion joints should be left at least every 15 ft and should amount to ½ to 1 in. Another method is to place a slip of thin cardboard between bricks in each vertical joint (or thicker pieces in alternate joints). These will burn out and allow each brick to expand freely, and yet there will be no general movement of the wall. Thin pieces of steel, which are pulled out as the wall progresses, have sometimes been used instead of the cardboard.

In the case of arches, there is often a pinching off of the tips due to temperature strains. Care, however, should be taken to see that there is clearance between the inner ends when temperature or load conditions are severe.

Failure due to heating wet brickwork rapidly is sometimes considered spalling. The remedy is obvious. Mechanical breakage when slicing off slag deposits is also classed as spalling by some people. The brick manufacturer can do little to help this failure except to supply the hardest bricks that will stand the temperature changes.

There has perhaps been too great a tendency for manufacturers and users of refractories to specify brick with a good spall-resisting quality, as judged by the laboratory test. Many cases have come up where a hard,

CHAPTER XVI

THE REACTION BETWEEN REFRACTORIES AND SLAGS OR GLASSES

1. Chemical Effect of Slag Action. In general, slag action can be divided into chemical effects and physical effects, the first of which will now be considered.

Equilibrium Conditions. It is very important to make a distinction between equilibrium conditions and the rate of reaction. For example, if an intimate mixture of magnesia and silica is maintained at a definite temperature, it will, after a certain length of time, be converted into mag-

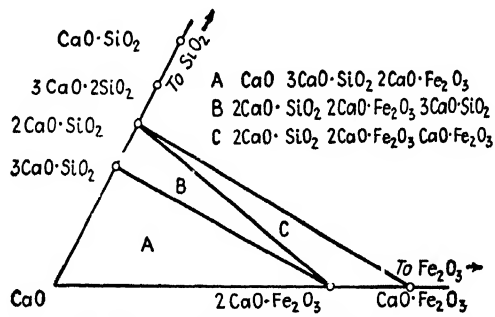


FIG. 272. Composition triangles in system CaO–SiO_2–Fe_2O_3. (*W. C. Hansen and R. H. Bogue, J. Am. Chem. Soc.*)

nesium silicate with a relatively low melting point. When the conversion is as complete as the proportion of the substances permits, equilibrium is attained and no further change will occur at that temperature. If the temperature is low, this reaction will progress with extreme slowness; but on the other hand, if the temperature is high, the reaction will take place rapidly; however, in each case, a state of equilibrium will be reached. It will first be advisable to investigate the equilibrium conditions for the combinations of various slags and refractories; for if the equilibrium conditions produce no material melting at a temperature lower than that at which the refractory is maintained, there can be no serious slag reaction. In such a case, the rate of reaction would not concern us. Usually, however, the slag or the material produced by the reaction of the slag with the refractory melts at a lower temperature than that maintained in the furnace.

Owing to the great complexity of the materials entering into slag and glass reactions, we do not have very complete information on the equilibrium diagrams concerned in these reactions. More data of this type are greatly needed. However, it can be stated in general that the slag reaction depends upon the formation of a low-melting compound or mixture.

Composition of Slags and Glasses. Table 83 shows typical analyses of commercial slags and glasses. In general, each one has so many elements present that it is difficult to tie them in with any simple system; and when the elements in the refractory are added, the complexity is still further increased.

Equilibrium Diagrams. It will be seen from Table 83 that the systems particularly applicable to slag-refractory reactions are

SiO_2—Al_2O_3—CaO (Fig. 224, Chap. XIII)
SiO_2—Fe_2O_3—CaO (Fig. 272)
SiO_2—CaO—Na_2O (Fig. 273)

It should not be forgotten that small amounts of some other materials such as PbO or F may greatly influence the slag action.

Rate of Reactions. The second factor in slag reactions is the rate at which reactions occur. Suppose that a refractory is washed by a slag capable of combining with the refractory to form a low-melting compound. If the reaction occurs rapidly, these low-melting compounds will be formed in considerable quantities and will run off the face of the wall, thereby exposing fresh surfaces for the attack of the slag; therefore the slag resistance of the refractory will be poor. On the other hand, let us suppose that the same low-melting-point compounds are formed but that the rate of reaction is slow. Then the compounds will be formed in small quantities, and the resistance of the refractory to the slag may be good. This is the reason why the prevalent idea that basic refractories must be used with basic slags and acid refractories with acid slags is not necessarily true. Although the acidic and basic qualities determine the formation products, they do not necessarily determine the rates of reaction. For example, magnesite will stand up well under the action of certain highly siliceous slags, and silica bricks are known to give good service in lime kilns under highly basic conditions.

The rate of reaction is greatly influenced by the temperature. In many instances, an increase of 10°C (18°F) will double the rate of reaction. This is the principal reason why certain refractories will resist slag very well at the usual working temperatures but will be rapidly eaten away if the furnace temperature is increased by 50°C (about 90°F). Unfortunately, practically no information is available, owing mainly to the experimental difficulties, on the rate of reaction of the materials in which we are

TABLE 83. ANALYSES OF TYPICAL SLAGS AND GLASSES

	Portland cement clinker	Lead blast furnace	Copper reverberatory	Coal ash, Ind.	Coal ash, Ill.	Acid, open hearth	Basic, open hearth	Blast furnace	Heating furnace	Window glass	Opal glass	Borosilicate glass	Fuel oil
SiO_2	21.9	32 6	47.4	42	43	50.1	23.3	36.8	17.0	72.10	65.8	80.6	44.0
Al_2O_3	5.6	3.1	29.0	15	17	3.0	0 3	11.7	3.9	0.80	6.6	2.0	1.3
Fe_2O_3	4.6	30.4*	34.5*	33	27	30.3*	26 6*	3.4*	75.3	0.08		0.2	
TiO_2					1	1.5	1.0	0.5	0.7				27.7
CaO	65.8	19 1	9.4	3	7	2 3	38 0	43.4	0.8	9.10	10.1	0.2	22.5
MgO	1.4	1.8	1.4	Trace	1	0.9	7 0	2.5	0.1	1.30		0.3	
MnO		0.9	0.4			11.7	4.2	0.9	1.9				
Na_2O										16.20	3.8	3.8	
K_2O				7	4	Trace	0.1	0.6	0.1		9.6	0.6	3.3
V_2O_5													1.0
ZnO		8 3	1.5										
CuO		0 2	0.5										
PbO		1 2	0 3										
SO_2	0.2									0.5			
As_2O_5										Trace		0.7	
F											5.3		

*Chiefly FeO.

interested at high temperatures. However, the reaction rate may be approximately expressed by the following equation of Arrhenius:

$$\log \frac{K_{t_2}}{K_{t_1}} = A\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where K_{t_1} = the reaction velocity at temperature T_1, deg abs
K_{t_2} = the reaction velocity at temperature T_2, deg abs
A = a constant of the reaction

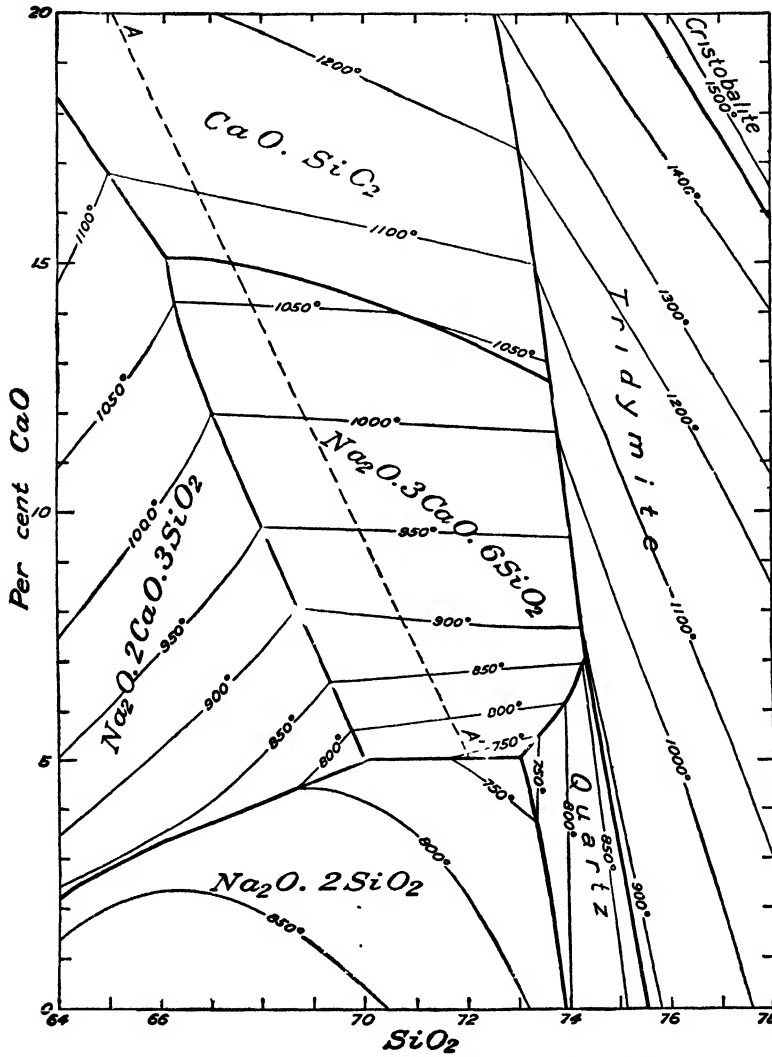


FIG. 273. Part of the ternary system Na_2O–CaO–SiO_2. (*Hall and Insley.*)

The value of A varies but is in the neighborhood of 10,000 for clays and fluxes.

2. Physical Effects of Slag Action. *Velocity of Flow.* As the rate of reaction is dependent upon the concentration of the slagging material on the surface of the refractory, it is evident that the more rapid the movement of the liquid slag over the refractory surface the more rapidly the fresh slag will be presented to the surface. It is well known that a liquid may flow in two ways. The first is a streamline flow, where the direction of the flow is parallel to the surface over which it is flowing; and the second, a turbulent flow, where the particles of the liquid are undergoing motion in various directions. The transition from streamline flow to turbulent flow depends upon the size, velocity, and viscosity of the melt. It is evident that turbulent flow is much more effective in bringing fresh slag to the surface than is streamline flow; so it is desirable to keep the velocity of flow low and the viscosity high. As the viscosity is dependent upon the temperature, we have another reason why high temperatures promote more rapid slag reaction. It may be said that in general, all slag flows are of the streamline type where the slag is flowing in thin layers over the refractory but, in the cases where the slag is in large quantities, as in glass tanks, the flow may be of the turbulent type for the more fluid glasses.

Diffusion in the Melt. Another physical effect that has an influence on the rate of slag attack is diffusion through the molten slag. Very little is known about the rate of diffusion of substances at high temperatures, but it is possible that this effect is quite important in bringing the reacting substances together. Bowen has shown that the rate of diffusion of silicates of the type of diopside in each other at 1500°C (about 2730°F) is comparatively rapid. The rate of diffusion is proportional to the viscosity and therefore depends largely upon the temperature of the melt.

Gas Diffusion through Melt. Sosman has suggested that another type of diffusion may have considerable influence on slag action. This is the phenomenon of the diffusion of gases through the melt. It has been shown that hydrogen and helium will pass through vitreous quartz glass at high temperatures so rapidly as to assume the character of an actual flow of gas.

Slag Penetration. In the previous discussion, we have considered the reaction occurring between the surface of the refractory and the molten slag. If the refractory is a dense material, this surface will be smooth; but on the other hand, if the refractory is porous, the surface may be considerably increased owing to penetration of the slag into the pores. A number of refractories are made from a hard grog and a softer bond, in which case the slag will react with the bond more rapidly than with the grog particles and will allow the latter to project from the surface. It often happens that these grog particles are carried away in the melt before they have

become dissolved. This has been noticed in glass melts and, of course, is harmful to the glass. Other types of refractories, even though composed of homogeneous material, will allow the rapid penetration of the slag into the interior.

Recent results on glass-tank blocks have shown that a high porosity may not cause susceptibility to slag action, provided the pores are all below a size that will allow the slag to be drawn in by capillary forces. On the other hand, flaws, laminations, or cracks are very harmful and allow rapid slag penetration.

Wetting of the Surface by Slag. There is another side to slag reactions which has not, it is believed, been generally discussed, *i.e.*, the wetting of the refractory surface by the molten slag. It has been noticed that when certain slags are applied to some refractories, they will melt on the surface and form in drops without wetting the surface. A refractory, under such conditions, is practically unaffected by the slag. This condition is just the opposite of many other cases, where the slag is drawn by capillary attraction deep into the pores. It seems quite reasonable to believe that the wetting by the molten slag in contact with the refractory may have a very important influence on the slag resistance of that refractory, and data on the surface tension under these conditions would be of considerable value.

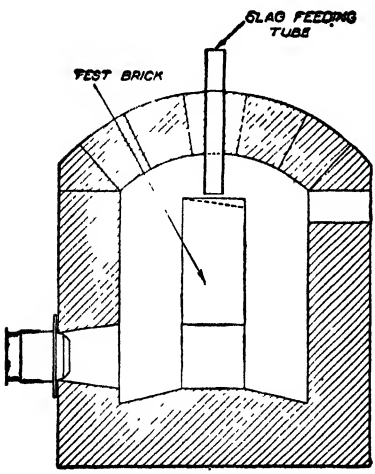


FIG. 274. Slag-test burner.

3. Laboratory Slag Tests. Of all laboratory tests for refractories, the least satisfactory is the slag test, for it is difficult in a reasonably short time to evaluate the resistance of a refractory. To accelerate the action by higher temperatures or by a greater flow of slag may materially alter the conditions of reaction.

Early Methods of Test. Some of the proposed methods of slag testing consisted in measuring the penetration of slag into the refractory, the fusion point of powdered slag and refractory when mixed together, and the petrographic study of mixtures of slag and refractory after definite heat-treatments. These methods measure some factors of slag reaction but not by any means all of them.

Refractory in Slag Baths. A number of experimenters have measured the resistance of a refractory to slags by suspending them in a bath of molten slag, with motion to bring new slag to the surface. The test of

Endell, Fehling, and Kley[10] used this method with considerable success.

Running Slag Test. Another method suggested by Prof. G. B. Wilkes consists of heating a single brick or a column of bricks to a uniform temperature and regularly dropping powdered slag on top, allowing it to run down the face in a groove, as shown in Fig. 274. The depth to which this groove has been cut at the end of the test gives a very good indication of

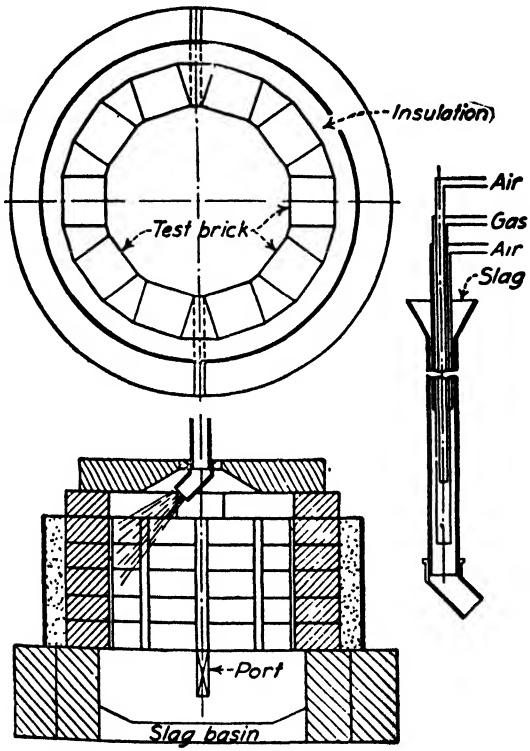


FIG. 275. Slag-test furnace and burner.

the slag resistance of the brick, because the test is carried on under conditions closely approximating those of service. Although this test gives excellent relative values, it is not a quantitative test and does not maintain a proper temperature gradient from the slag surface to the other face. Hartmann[18] used a similar method with a small specimen in an electric furnace.

Spray Slag Tests. Perhaps one of the most satisfactory tests consists in spraying powdered slag against the heated refractory. A number of experimenters have used this method, but the most practical furnace is that used by Hursh[21,32] as shown in Fig. 275. Here the powdered slag is

fed through a revolving burner impinging on the test bricks set on the inside of the cylindrical furnace. Thus, all the bricks get the same treatment and the temperature gradient through the bricks is similar to that found in service. If the test is run for several days, truly quantitative values can be obtained.

Tanks for Testing Glass Refractories. The only really satisfactory way to test glass-tank blocks is to use them in a small tank that is fed and drawn at regular intervals. A satisfactory tank for this purpose, shown in Fig. 276, is about the minimum size that can be used successfully. A 2-weeks'

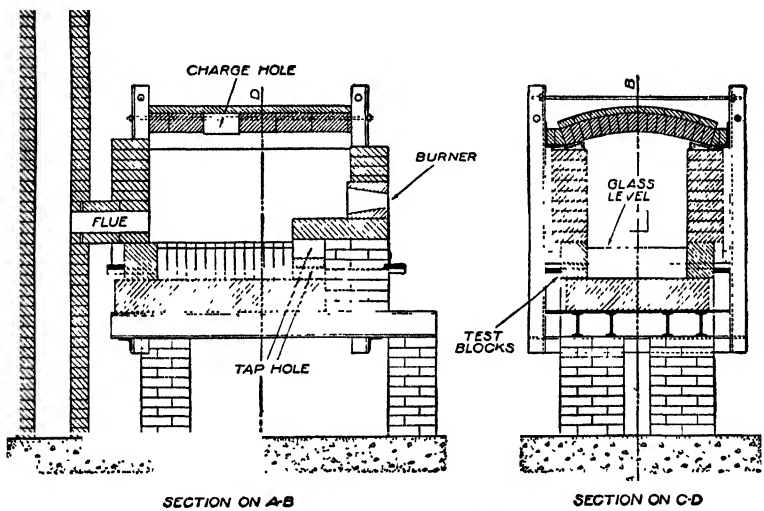


FIG. 276. Small tank with a 3 × 5 ft melting chamber. (*Courtesy of the Babcock and Wilcox Company.*)

run will give a fair indication of the resistance to the glass, but a longer run is sometimes desirable. McMullen[111] describes a small test tank for glass tank blocks that is heated by globars.

4. The Slag Resistance of Refractories. There are so few really quantitative data on the resistance of refractories to slags that it would seem impossible at the present time to give a table of values that would mean very much. However, from our experience in the use of refractories, certain conclusions can be drawn, which will be discussed in Part IV.

5. The Products Formed in Slag Reactions. *Fireclay Refractories and Coal-ash Slag.* The microscopic examination of the boundary layer between the slag and refractory indicates several definite zones that are generally present in all slagging of this nature. A study of these conditions has been made by McDowell and Lee,[117] McVay and Hursh,[118] and others. On the furnace side, there is a layer of slag that at high tem-

peratures may be very thin, perhaps 1 mm, but at lower temperatures may build up to a coating of several centimeters. This layer of slag usually contains anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$, associated with iron oxide, which may be in any of several forms, depending upon the atmosphere of the furnace as shown in Fig. 277. Mullite crystals are also present, but they usually contain iron oxide in solid solution.

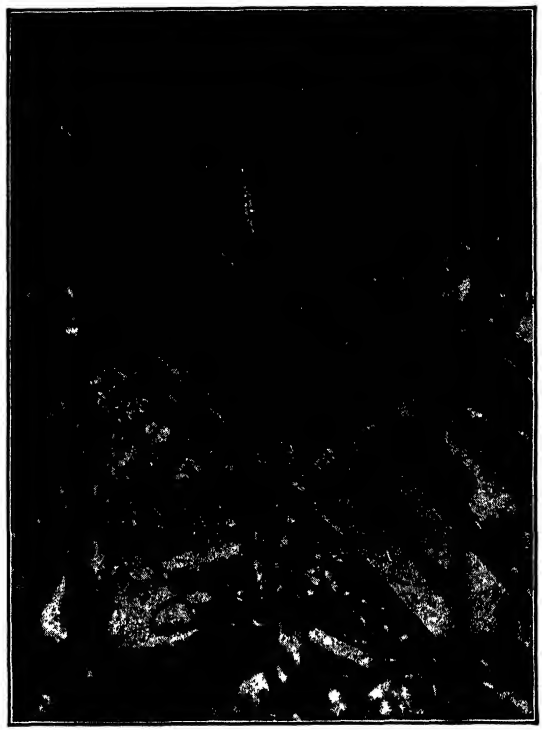


FIG. 277. Thin section of Illinois coal-ash slag which was slowly cooled. The large crystals shown is feldspar; 250 diameters, with crossed Nicol prisms and a gypsum plate.

The next zone, which is the transition zone between the slag and refractory, contains mainly large and well-developed mullite crystals. As in nearly every case of slagging between firebrick and slag or glass, the development of mullite crystals is accelerated in this intermediate zone.

The next zone is in the body of the refractory itself and generally shows some penetration of the slag into the pores of the brick and, in many cases, the initial solution of particles of the refractory.

In the case of a firebrick crown that is swept by powdered slag, stalactites form and drip off the roof. Here the composition may be somewhat different from the slag on the side walls because more time is available for

equilibrium to be established before the slag runs off. An examination of the stalactites shows magnetite and anorthite crystals well developed; and in a few instances, mullite crystals have been observed.

High-alumina Refractories and Coal-ash Slag. Refractories containing a high percentage of mullite, which have been made from kyanite and diaspore, show somewhat different characteristics under the action of slag.

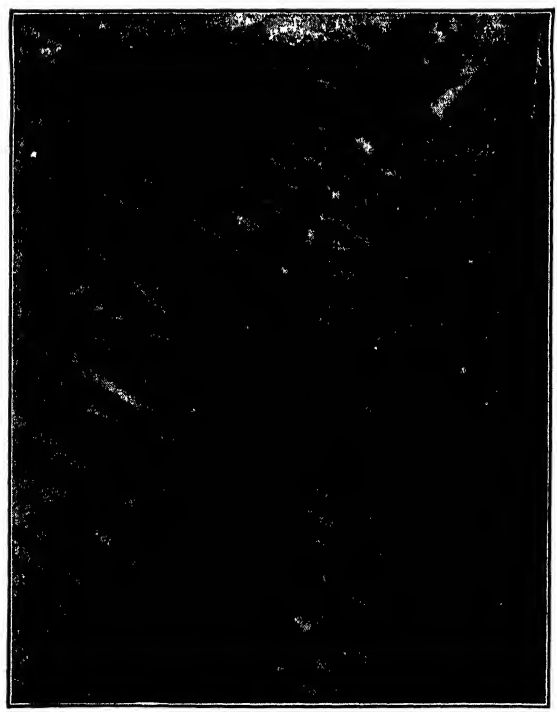


FIG. 278. A thin section of a sample of opal glass which was near the refractory, showing dendritic crystals of cristobalite; 1,200 diameters, with ordinary transmitted light.

The first characteristic that will be noticed is that the slag penetrates deeply into the refractory and leaves little on the surface. On the surface of the refractory, which is only lightly covered with slag, mullite crystals predominate; but as we penetrate farther into the body of the refractory, corundum crystals increase in number until they may be equal in volume to the mullite. The zone of corundum crystals seems to give a weaker structure than the zone of interlocking mullite crystals and may present a zone of weakness that will cause spalling. The formation of the corundum crystals indicates a more rapid solution of the silica than of the other constituents, leaving excess alumina behind.

Siliceous Fireclay Refractories and Soda-lime Glass. The constituents formed between refractories and glass have been examined by Insley,[89] Wilson,[87] and Kai-Ching-Lu.[102] The hottest zone between the glass and the refractory is generally milky white or brownish and contains cristobalite crystals in glass. Corundum plates and nephelite crystals are sometimes observed here. The next zone as we approach the refractory is a white

FIG. 279. Thin section of opal glass taken at a point very close to the refractory. A large number of dendritic cristobalite crystals and a few corundum crystals are seen. A few unidentified crystals of high index are present in this slide; 80 diameters, with ordinary transmitted light.

layer containing mainly mullite crystals. The refractory itself shows penetration of the glass into the pores, but this is not evident at any distance from the surface. Thin sections shown in Figs. 278 to 281 give a clear picture of the crystal formation in glass.

Aluminous Fireclay and Soda-lime Glass. In this case, the hottest zone is a brown layer containing soda-lime feldspars imbedded in glass. The next layer is white and consists of mullite crystals imbedded in alumina glass with corundum crystals. The latter are formed from the alumina-saturated glass in this zone.

Silica Brick and Iron. A careful examination of silica roof brick by Scott[129] shows the following characteristics: The hot end of the brick is a gray zone of cristobalite crystals and magnetite, with perhaps a few tridymite crystals at the cooler end; the next cooler zone is black and consists of tridymite, magnetite, and a small percentage of cristobalite; the cooler

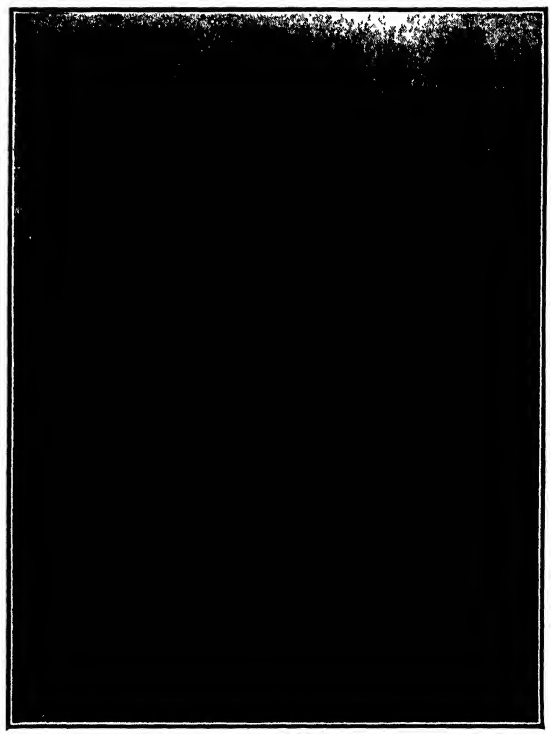


FIG. 280. Thin section of a glass stone, composed of nephelite which was formed by materials dropping from the crown into the melt. The material at the lower left-hand corner, containing inclusions, is the nephelite. The long slender needles appearing at the edge of the stone are of feldspar; 265 diameters, with crossed Nicol prisms and gypsum plate.

end of the brick consists of cristobalite, tridymite, and quartz, the last increasing toward the outer end of the brick.

In the hearth, fayalite, Fe_2SiO_4, and tridymite were found in a brown glass. In the hotter portions, some cristobalite was found and about 20 per cent ferrous oxide was generally present. Iron silicates do not usually form in large quantities but were present only where the conditions were reducing.

Magnesite and Iron. In general, magnesite in contact with iron or its oxides gives periclase crystals with iron in solid solution, together with

some crystals of magnesioferrite. When lime is present, calcium oxide crystals are formed, sometimes of large size. Crystals of tricalcium silicate have been observed.

Zerfoss and Davis[134] give an excellent discussion of the theories of bursting when chrome-magnesite brick comes in contact with iron oxide.

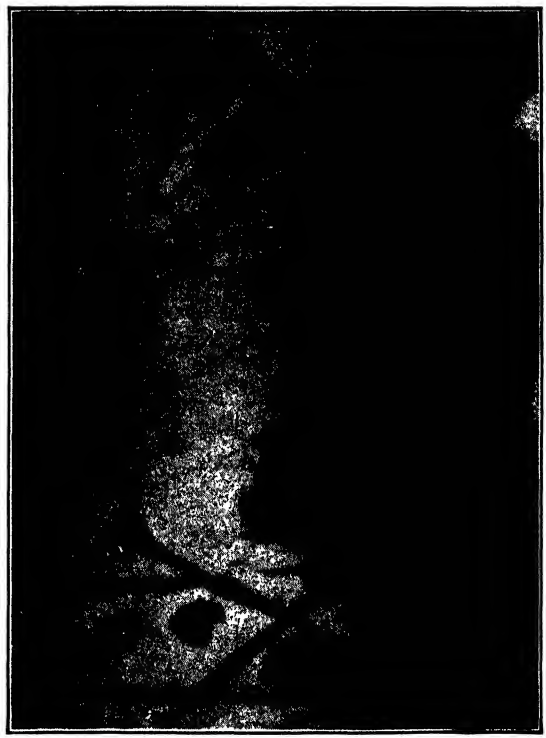


FIG. 281. Thin section of a stone in a glass melt. This stone was caused by a particle of the refractory being eroded from the side of the glass tank; 500 diameters, with crossed Nicol prism and gypsum plate.

They conclude on the basis of their work that the chromite grains act as nuclei for the growth of Fe_3O_4 and that this growth causes the bursting.

Fireclay Refractories and Iron. The main constituents formed by this reaction are iron silicates and mullite, with iron in solid solution.

Alkali Vapors and Refractories. Alkali vapors or dust are encountered in many industrial furnaces such as glass tanks, boiler furnaces, and blast furnaces. Much work has been done in the last few years on this subject as shown by the references.[67-86] Siliceous-type bricks are not so resistant to alkali vapors as fireclay or aluminous types of brick, owing to the formation of a liquid slag in the first case. According to Hartmann,[76] magne-

site brick are very resistant. Hard firing and low porosity increase the slag resistance of any brick.

Other Slags. The reaction between refractories and other slags has not been studied to any great extent. Audley[135] examined the zinc-fireclay reaction and found the occurrence of a zinc spinel. Turner[95] and McSwiney[137] have discussed the action of arsenic in glass on refractories, but no definite conclusions have been reached.

We need information on the products formed by copper, lead, and tin when in contact with various refractories. Little is known of the slag reactions with chromite, zirconia, and zircon.

FIG. 282. Slag erosion of a boiler furnace wall. (*Courtesy of Commonwealth Edison Company.*)

6. Gases and Refractories. *Carbon Monoxide.* It has been known for a number of years that CO gas at certain temperatures weakens the structure of a firebrick. This effect is particularly noticeable in blast-furnace linings and zinc retorts. A number of investigators have studied the problem, such as Mitra and Silverman,[39] Hubbard and Rees,[40] and many others listed in the references. In general, it is believed that the starting point of the disintegration is the ferric oxide spots in the refractory. The ferric oxide is reduced to ferrous oxide, which acts as a catalyst to break up the CO to CO_2 and C, forming a deposit that causes the disintegration. This reaction takes place only between 420 and 470°C (788 to 878°F). It is believed by Mitra and Silverman that the magnetic oxide of iron Fe_3O_4 is not susceptible to this action.

A brick to resist CO must be either very low in iron or fired at a temperature high enough to allow the iron to combine with the silica and alumina in the brick.

Hydrocarbon Gases. A number of investigators have studied the embrittling effect of hydrocarbon gases on fireclay brick in the cracking

FIG. 283. Detail of typical slag erosion. (*Courtesy of Commonwealth Edison Company.*)

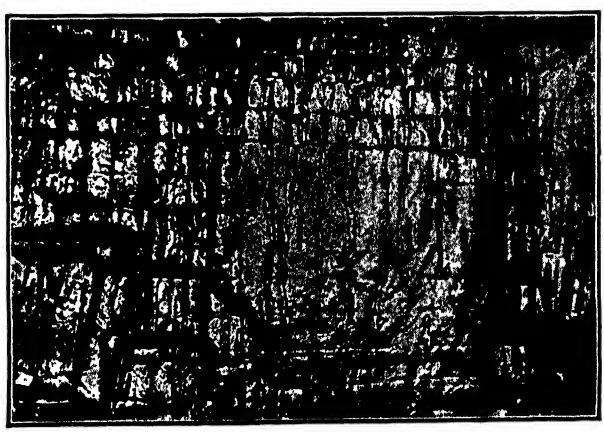


FIG. 284. Detail of slag erosion. Note the grooving effect. (*Courtesy of Commonwealth Edison Company.*)

range of temperature.[50,52,56,57] The action seems to be similar to that of CO, *i.e.*, a deposition of carbon.

Steam. In some cases as in water-gas generators, steam has shown a weakening influence on refractories.

Oxygen. Silicon carbide refractories have a tendency to oxidize slowly. Many efforts have been made to prevent this by glazing the sur-

face as described by Walton[45] or by removing catalytic agents as described by Hartmann.[43]

Chlorine. Richardson[64] shows that chlorine forms volatile ferric chloride, which tends to purify and in some cases weaken the refractory. Owing to the iron removal, their resistance to CO increased.

7. Reaction between Different Refractories in Contact. It is often desirable to know the maximum safe temperature at which one refractory can be heated when set on another. Our available data are not very extensive, and many factors, such as purity and atmosphere, have not been under complete control. However, Table 84 gives some data on commercial refractories, and Table 49, in Chap. X, gives data on pure materials.

TABLE 84. INITIAL REACTION TEMPERATURES, °F

Material	Zircon	Zirconia	Magnesite	Silicon carbide	Chrome	Forsterite	Fused alumina	Kaolin	Superduty
Zircon[146]		3300							
Magnesite[145]	2800		None	2800	>2800	>2800	>2800	2500–2600	2500–2600
Zirconia							3300		

Remmey[145] points out that in some specimens, such as a 91 per cent alumina brick, the glassy phase may become sufficiently fluid at high temperatures to drain out of the brick and leave nearly pure alumina behind.

8. Slag Erosion in Service. The deterioration of refractories by slag is very serious in many types of installation. The action is particularly severe in boiler furnaces where low-grade coal is burned, as the slag formed is a very active flux. In many cases, the only solution to the problem is to use air or water cooling. Although it might be possible to find a more resistant refractory than fireclay brick, such as magnesite or spinel, the rapid heating and cooling of the boiler furnace make the use of these easily spalled materials impossible. Efforts should be made in the design to minimize the flow of slag over the hotter surfaces.

In Figs. 282 to 286 are shown typical boiler-furnace walls that have been eroded by slag. The vertical grooves formed by the running slag are representative. Where the melting point of the ash is high or the temperature of the furnace is low, the ash will not flow but will form a protective coating on the wall. If this coating does not build up so thickly that it tears off the face of the wall, it serves as a protection to the refractory.

The slag erosion in forging and heating furnaces by the molten mill scale is serious in the bottoms. Magnesite and chrome bottoms have been tried with considerable success under these conditions (Fig. 287).

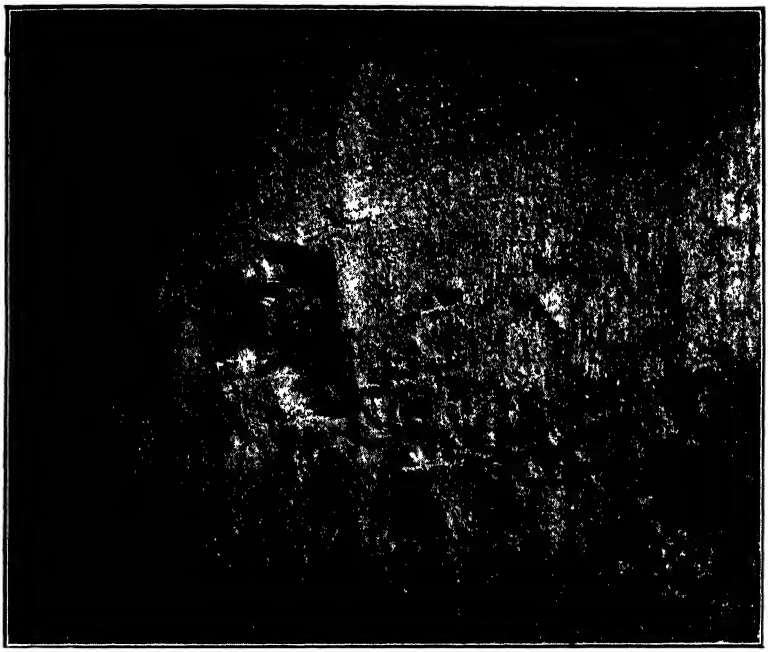


FIG. 285. A wall coated with a high-fusion-point slag. (*Courtesy of Stone and Webster.*)

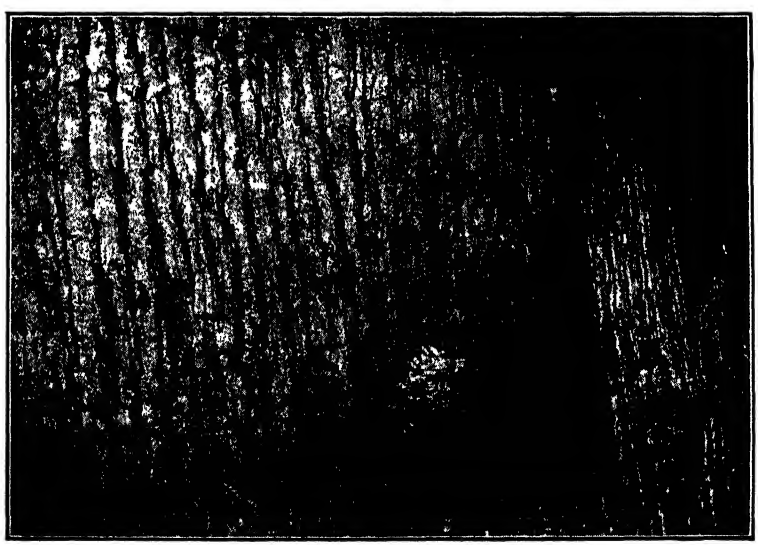


FIG. 286. Bad grooving by slag on an inclined wall. (*Courtesy of L. E. Hankison.*)

In steel- and iron-melting operations, the high temperatures and activeness of the slag make the conditions for the refractory very severe. In the open hearth, the continued high temperature allows the use of magnesite or silica bottoms. Where fireclay refractories are used, as in the cupola, frequent patchings are necessary. High-alumina refractories seem to show good service in cement kilns (Fig. 288).

FIG. 287. Thin section of magnesite refractory which was used in a high-temperature furnace. The dark material in this section is magnesite which contains a considerable amount of iron rendering it fairly opaque. The light-colored crystals which can be seen are the result of the action of the slag on the magnesite; 60 diameters, with crossed Nicol prisms and gypsum plate.

Glass tanks are maintained at an even temperature, and rather large blocks of fireclay refractory are generally used. However, the blocks are eaten away fairly rapidly at the metal line. The action of some glasses is much more severe than others. Not only is it important to have a long life for the blocks, but it is necessary to have a material that will not form seeds or stones in the glass. The erosion of a typical glass tank is shown in Fig. 289 where the grooving of the blocks is evident. Recently, good results have been obtained with fusion-cast blocks having a high-mullite content and low porosity. The physical characteristics of the block may perhaps be more important than the chemical composition.

FIG. 288. Thin section of a refractory used in a rotary cement kiln. The charge has reacted to some extent with the refractory and partially eroded it, with the formation of lime feldspar. These are the light-colored crystals which appear between the grains; 250 diameters with crossed Nicol prisms and gypsum plate.

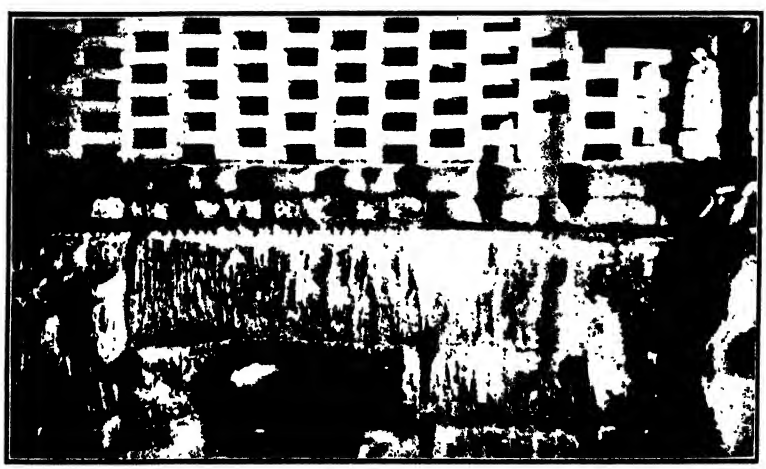


FIG. 289. Erosion of a typical glass tank.

CHAPTER XVII

EXPANSION AND SHRINKAGE

1. Methods of Measurement. A number of different methods have been employed to determine the coefficient of thermal expansion of materials up to high temperatures. A few of the more satisfactory ones will be described.

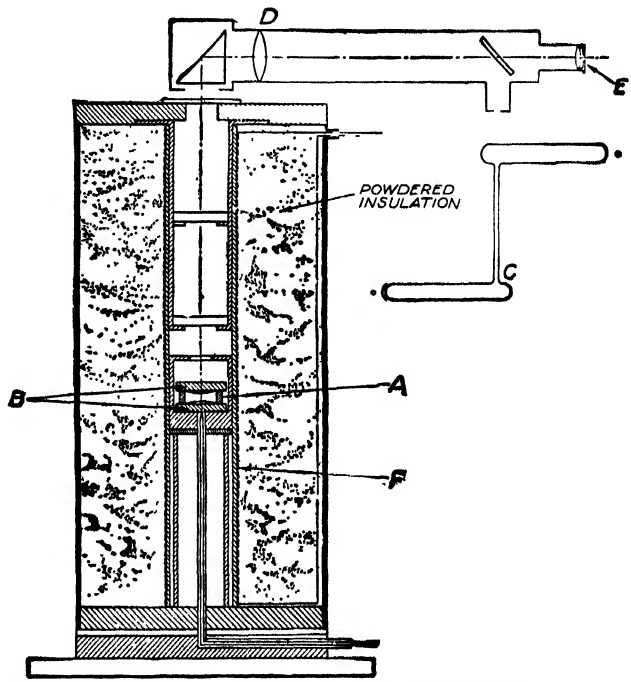


FIG. 290. Measurement of expansion with the Fizeau interferometer.

Interferometer Method. Where it is necessary to use a very small specimen, such as a section of glaze or enamel, the interference method, best illustrated by the Fizeau interferometer,[9,45,62] is perhaps the most accurate. A cross section of this instrument is shown in Fig. 290. The specimen *A* can be in the form of a short cylinder or in three struts of equal length separating two fused quartz disks *B*, which have been polished with optically plane surfaces. Light from the vacuum tube *C* is passed through the optical system *D* and down through the quartz-disk assembly. Light is reflected from the surfaces in contact with the specimen, and the resulting

beam is passed back through the optical system to the eyepiece *E*. A series of alternating dark and light bands are produced by interference. The position of these bands is dependent upon the relative distance between the two quartz disks, and each band represents a distance of one-half wavelength of the particular light used. Of course, the more nearly parallel the plates the broader will be the bands.

When a test is made, the specimen is put in place and the instrument carefully lined up until the bands appear in the field. The heater *F* is turned on, and the temperature slowly raised to any desired value while the number of bands passing a vertical cross hair in the eyepiece are counted. From the number of bands and the wavelength of the light, the coefficient of thermal expansion of the specimen can be readily computed. The upper temperature is limited by this method to about 1000°C (about 1830°F). Discs of sapphire would permit going to temperatures of 1700°C (about 3090°F).

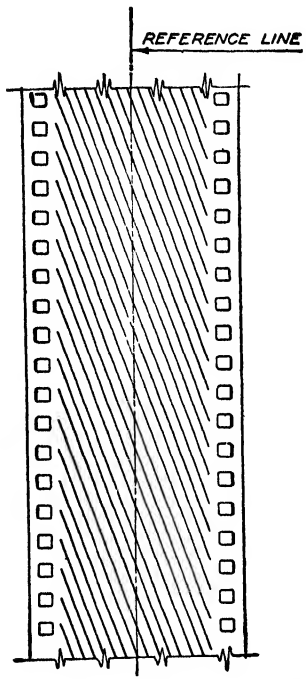


FIG. 291. Interference bands taken on a moving-picture film.

Counting the passage of the bands visually is a tedious process. Also there is the danger of missing one or more bands. Recently, several devices have been used to simplify the observation. In one case, an image of the bands and crossline is thrown on a moving strip of film, giving a set of lines as shown in Fig. 291. The number of lines and fractions crossing the reference line can readily be counted. Another method consists of using several band systems from sources having different wavelengths. By an initial and final reading on three sets of bands, the expansion can be computed without a continuous count. Since considerable manipulative skill is required to obtain good results with this instrument, it is not adapted to general plant use.

Fused-quartz-tube Method. Another method, which will permit tests to be made at slightly higher temperatures, consists of forming the specimen into a small cylinder and placing it in a quartz tube surrounded by a heater. The expansion of the cylinder is transferred outside the furnace by a fused quartz rod, the movement of which is measured by a micrometer telescope or dial.[33] Expansions can be measured in this way to temperatures as high as 1100°C (about 2010°F).[3] Other experimenters have used fused-

quartz distance pieces to convey the movement to a dial micrometer. Such a device was used by Geller and Heindl.[19]

A similar method is used by Heindl[46] in a reducing atmosphere, where graphite can replace the fused quartz and thus allow the attainment of much higher temperatures. Distance pieces of whiteware body were used by Geller and Bunting.[66] Sapphire rods as distance pieces have permitted this method to be used to much higher temperatures.

High-temperature Measurements. When it is desired to obtain the coefficient of thermal expansion of a specimen at higher temperatures, a somewhat different procedure must be followed. A method developed at

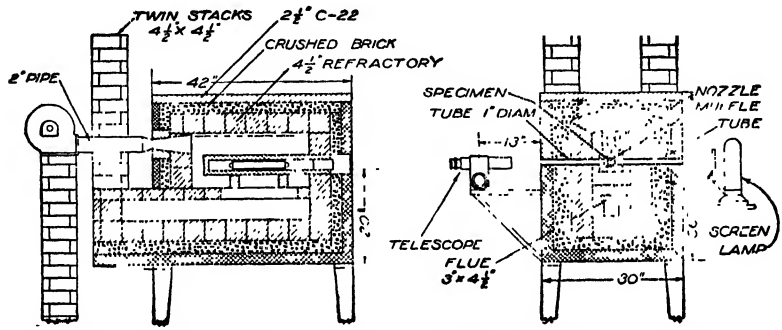


FIG. 292. Furnace used to measure the coefficient of expansion of refractories.

the Babcock & Wilcox laboratory[16] has proved quite satisfactory up to a temperature of 1700°C (about 3095°F). A specimen 9 in. long and 1 in. square is evenly heated, and its length measured directly with micrometer telescopes.

A drawing of the furnace is shown in Fig. 292. The specimen is placed on a level bed of loose sand composed of some refractory material, such as fused alumina. Around the specimen is a silicon carbide muffle, which ensures an even heating of the specimen. The heat is supplied to the furnace by a gas burner, the flame passing over the muffle and down around it to the exit flue and then out through the two stacks. Sight tubes pass through the furnace at the ends of the specimens and are cemented tightly to the walls of the muffle. The telescopes are sighted through these tubes across the ends of the specimen. Because of the excellent black-body conditions in the muffle, it would be quite impossible to distinguish the end of the specimen from the wall, so the sight tube is continued through on the other side of the furnace, and a powerful electric light with a ground-glass screen is placed at the end of the tube in order to provide a background brighter at all temperatures than the end of the specimen. The background must have an effective temperature higher than the highest

reached by the specimen in order to give contrast. The light should be used for all readings, for there is an apparent shift in the image when a dark background is used.

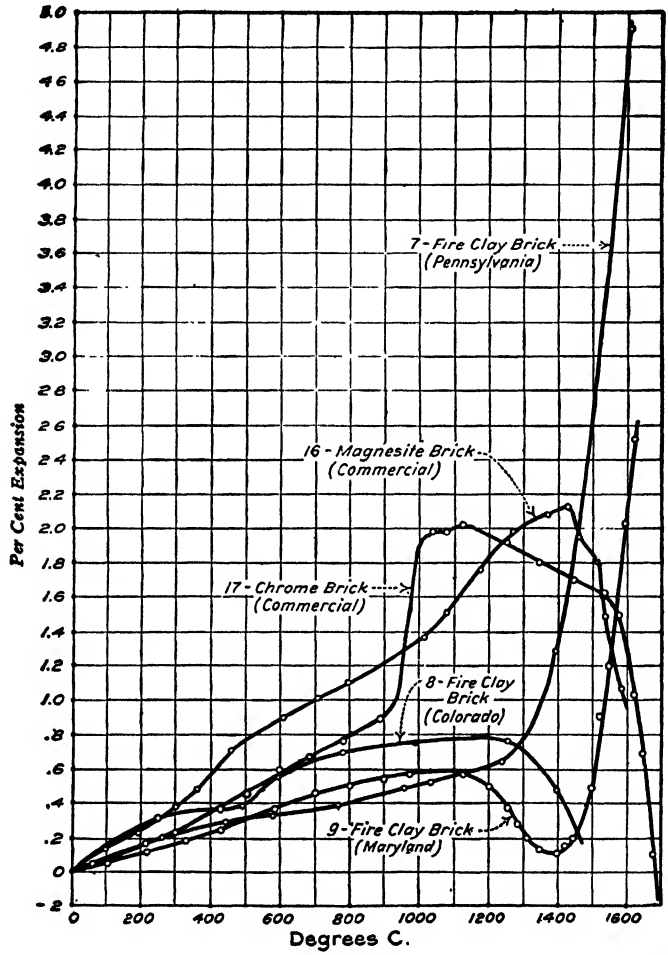


FIG. 293. Expansion curves for a number of refractories. (*J. Am. Ceram. Soc.*)

A specimen can be cut out of a standard brick with a carborundum saw; or where a brick is not available, it can be molded and burned.

To obtain an accurate reading on the end of the specimen, it is necessary to grind and polish it accurately. The telescopes contain vertical cross hairs which can be adjusted to correspond to the image of the specimen. The temperature of the specimen for the lower range is measured

with a thermocouple laid against the specimen. At high temperatures, this couple is pulled out and the temperature measured by an optical pyrometer through the sight tube. When making a test, it has been found most satisfactory to increase the temperature at a regular rate of 100°C per hr and to make measurements of the length as often as seems desirable.

This method will give a precision of measurement within ±0.01 per cent of the length of a specimen, and the temperature can be read to ±10°C (±18°F) up to the highest temperatures. The maximum temperature of this test is limited mainly by the reaction of the specimen with its support. If the expense of building a complete furnace of the test material is justified, this reaction could be prevented and temperatures as high as 1800°C (about 3270°F) could undoubtedly be reached.

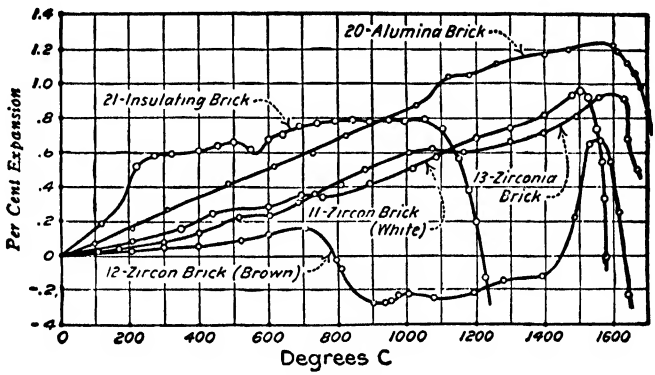


FIG. 294. Expansion curves for a number of refractories. (*J. Am. Ceram. Soc.*)

A similar type of furnace heated by globars is more convenient to operate and control than the preceding setup but is limited in maximum temperature to about 1600°C (about 2900°F).

The results from expansion tests are most conveniently plotted with the temperatures as abscissas and the percentage expansions as ordinates. From the slope of this curve, the coefficient of thermal expansion can be readily found at any temperature.

2. Expansion Characteristics of a Number of Refractory Bricks. In Figs. 293 to 297 are shown the expansion curves for a number of refractory materials. It should be kept in mind that the burning temperature markedly influences the curves, especially the temperature at which permanent shrinkage begins.

In Table 85 are summarized the main characteristics of many of these materials.

The data from expansion curves are of considerable value in determining the characteristics of a brick produced from a given material. It has

been shown that the tendency of a brick to spall, other conditions being invariable, is proportional to the coefficient of thermal expansion at the temperature where spalling occurs. This temperature range lies between 300°C (about 570°F) and 700°C (about 1290°F) in most cases; hence, the maximum coefficient of expansion in this range is a direct indicator of the spall-resisting properties of the material.

The expansion curves indicate in most cases where an allotropic change takes place in the crystal structure; *e.g.*, the curve for the silica brick shows

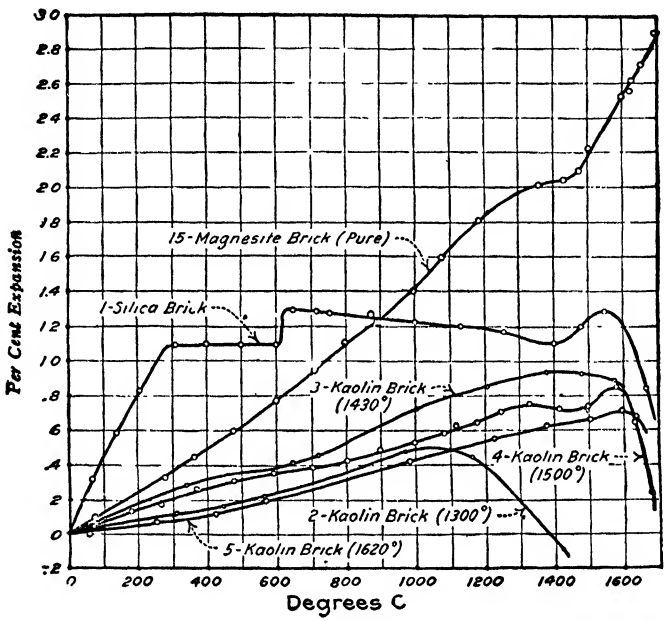


FIG. 295. Expansion curves for a number of refractories. (*J. Am. Ceram. Soc.*)

distinctly the inversion of low- to high-cristobalite around 260°C (500°F). The quartz inversion point is also sharply defined at 573°C (1062°F). The expansion of the specimen above 1470°C (about 2680°F) shows the gradual change of tridymite to cristobalite. The inversion point of quartz is shown to some extent in nearly all the fireclay bricks, indicating the presence of some free quartz in all these materials.

The temperature at which the specimen begins to shrink or expand irreversibly is of considerable importance, for it shows the approximate temperature at which the specimen is burned and also the maximum temperature at which it can be used satisfactorily in service.

The total reversible expansion of a material is of interest for the computation of the necessary expansion joints in the design of furnaces and kilns.

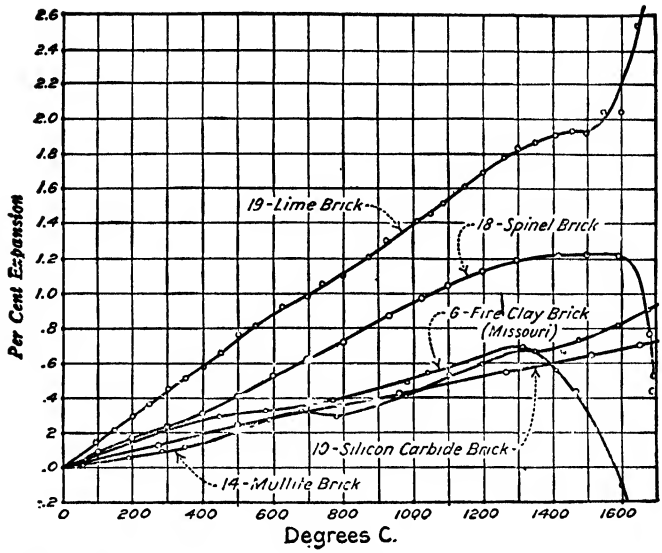


FIG. 296. Expansion curves for a number of refractories. (*J. Am. Ceram. Soc.*)

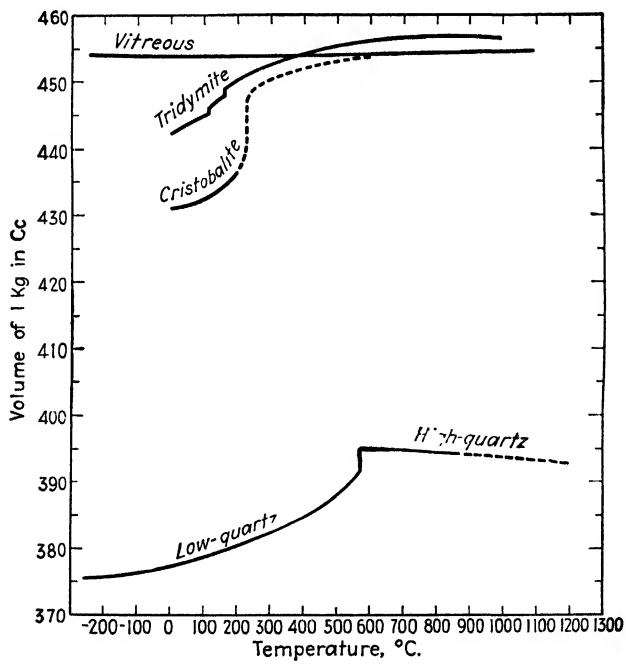


FIG. 297. Temperature-volume curves for the principal forms of silica. (R. B. Sosman, "The Properties of Silica," Chemical Catalog Company, Inc., Reinhold Publishing Corporation, New York, 1927.)

TABLE 85. THERMAL EXPANSION

Specimen No.	Brick type	Burning temperature		Mean coefficient of expansion between 0°C (32°F) and shrinkage temperature (per 1°C)	Maximum coefficient of expansion between 300°C (572°F) and 700°C (1292°F) (per 1°C)	Maximum irreversible contraction or expansion up to 1700°C (3092°F), per cent (— is expansion)	Inversion points		Temperature at which shrinkage or expansion begins	
		°C	°F				°C	°F	°C	°F
1	Silica			0.0000083	0.0001000	1	260 to 610	500 to 1130	1550	2822
2	Kaolin	1300	2372	0.0000047	0.0000079	1	260 to 600	500 to 1112	1050	1922
3	Kaolin	1430	2606	0.0000068	0.0000087	1	260 to 600	500 to 1112	1380	2516
4	Kaolin	1500	2732	0.0000053	0.0000070	1	260 to 600	500 to 1112	1580	2876
5	Kaolin	1620	2948	0.0000043	0.0000067	1			1610	2930
6	Fireclay (Missouri)			0.0000054	0.0000080	Large	600	1112	1300	2372
7	Fireclay (Pennsylvania)			0.0000051	0.0000064	−5	600	1112	1250	2282
8	Fireclay (Colorado)			0.0000054	0.0000174	Large	260 to 600	500 to 1112	1220	2228
9	Fireclay (Maryland)			0.0000045	0.0000080	−3			1100	2012
10	Silicon carbide			0.0000043	0.0000048	0			1700+	3092+
11	Zircon (white)	1650	3002	0.0000064	0.0000092	Large	800	1472	1510	2750
12	Zircon (brown)	1590	2894	0.0000042	0.0000048	2	600 to 1400	1112 to 2552	1550	2822
13	Zirconia	1675	3047	0.0000059	0.0000087	1	800 to 1150	1472 to 2102	1600	2912
14	Mullite	1785	3245	0.0000053	0.0000082	0	780 to 1350	1436 to 2462	1700+	3092+
15	Magnesite (pure)	1680	3056	0.0000142	0.0000151	0	1430	2606	1700+	3092+
16	Magnesite (Com'l)			0.0000147	0.0000210	2			1440	2624
17	Chrome (Com'l)			0.0000104	0.0000124	2	1000	1832	1540	2804
18	Spinel	1690	3074	0.0000076	0.0000110	1			1600	2912
19	Lime	1740	3164	0.0000138	0.0000145	0	1500	2732	1700+	3092+
20	Alumina	1650	3002	0.0000077	0.0000082	1	1180	2156	1580	2876
21	Insulating			0.0000074	0.0000480	Large	200 to 570	500 to 1058	1050	1922
22	Zircon (electrically fused)			0.0000042	0.0000140					
23	Magnesite (electrically fused)			0.0000102	0.0000120					
24	Topaz	1675	3047	0.0000043	0.0000151					
25	Zircon (purified)			0.0000038	0.0000151					

The effect of burning temperature on the coefficient of thermal expansion of clays is illustrated by the curves for kaolins. At the lowest temperature, the coefficient is low owing to the small amount of mullite development and corresponding small silica formation. Only a slight trace of the silica inversion points is present. At a burning temperature of 1430°C (about 2600°F), the thermal-expansion coefficient is much higher and the inversion points are quite prominent as a result of the breaking down of the silicates to form mullite and some free silica. At 1500°C (about 2730°F), the coefficient is reduced because of the initial combination of the free silica into glass. At 1620°C (about 2950°F), the free silica has almost entirely changed to glass, giving a low coefficient.

It may be concluded that magnesite, chrome, and lime have high mean coefficients of thermal expansion. Silica, alumina, and spinel have intermediate values, whereas clays, zirconia minerals, mullite, and silicon carbide generally have low values. In regard to the coefficient of expansion in the spalling range, silica shows much the highest value. Magnesite, chrome, lime, and spinel also have high values, as their sensitiveness to spalling would lead us to believe. Clays, alumina, mullite, zirconia minerals, and silicon carbide have lower values.

The more recent results of Heindl[46] made in a reducing atmosphere are substantially the same as those given here, except in the case of chromite where a difference was noted.

3. Expansion of Silica Minerals. The thermal-expansion characteristics of the various forms of silica are of interest, because the inversion points are clearly shown. An expansion curve of a silica refractory will indicate roughly the constituents present. In Fig. 297 are shown expansion curves of the four forms of silica. The low expansion of the quartz glass and the sudden changes at the inversion points are noteworthy. All the high-temperature forms of silica have a low coefficient of expansion.

The volume of all forms of silica is comparatively constant above 600°C (about 1100°F); therefore no spalling troubles will be encountered if the furnace is never allowed to fall below this temperature. Open-hearth steel furnaces, for example, which are constructed to a considerable extent of silica brick, experience large and sudden temperature changes. The temperature, however, is never allowed to fall below 600°C (about 1100°F) or 800°C (about 1470°F) even for repairs.

Unfortunately, quartz glass is not stable above about 1200°C (about 2190°F). If it were, a refractory extremely resistant to temperature changes could be made of it.

4. Expansion of Other Refractory Materials. In Table 86 are given the coefficients of thermal expansion of a number of other refractory materials. It should be remembered that zirconia has a transformation at 1000°C

TABLE 86. COEFFICIENT OF THERMAL EXPANSION OF HIGH-FUSING CRYSTALS

Material	Temperature range °C	Temperature range °F	Coefficient of thermal expansion per °C	Authority
Alumina, fused, recrystallized	25–800	77–1472	7.9×10	Merritt[9]
Sapphire, ‖ principal axis	20–1000	68–1832	9.0	Austin[40]
Sapphire, ⊥ principal axis	20–1000	68–183[illegible]	8.3	Austin[40]
Magnesium oxide, fused	25–800	77–1472	13.4	Merritt[9]
Magnesium oxide, single crystal	25–1000	77–1832	13.8	Austin[40]
Mullite, aggregate	20–1430	68–2552	5.3	Heindl[46]
Mullite, ‖ principal axis	20–1000	68–1832	5.7	Austin[40]
Mullite, ⊥ principal axis	20–1000	68–1832	4.5	Austin[40]
Zircon, ‖ principal axis	20–800	68–1472	6.2	Austin[40]
Zircon, ⊥ principal axis	20–800	68–1472	3.7	Austin[40]
Zirconia, ‖ principal axis	25–800	77–1472	8.1	Merritt[9]
Zirconia, ⊥ principal axis	25–800	77–1472	7.3	Merritt[9]
Zirconia, aggregate	25–800	77–1472	6.2	Merritt[9]
Zirconia, ‖ principal axis	20–900	68–1652	5.7	Austin[40]
Zirconia, ⊥ principal axis	20–900	68–1652	8.9	Austin[40]
Chromite, single crystal	20–1000	68–1832	8.1	Austin[40]
Thoria, aggregate	25–800	77–1472	9.3	Merritt[9]
$ZnO \cdot Al_2O_3$, aggregate	25–800	77–1472	8.9	Chesters and Parmelee[50]
$MgO \cdot Al_2O_3$, aggregate	25–800	77–1472	8.0	Chesters and Parmelee[50]
$FeO \cdot Al_2O_3$, aggregate	25–800	77–1472	8.6	Chesters and Parmelee[50]
$MnO \cdot Al_2O_3$, aggregate	25–800	77–1472	7.1	Chesters and Parmelee[50]
$ZnO \cdot Cr_2O_3$, aggregate	25–800	77–1472	10.1	Chesters and Parmelee[50]
$Mgo \cdot Cr_2O_3$, aggregate	25–800	77–1472	9.3	Chesters and Parmelee[50]
$FeO \cdot Cr_2O_3$, aggregate	25–800	77–1472	8.5	Chesters and Parmelee[50]
$BaO \cdot Al_2O_3$, aggregate	25–1000	77–1832	7.5×10	Henry[78]
$2BeO \cdot SiO_2$, aggregate	25–1000	77–1832	6.4×10^{-6}	Henry[78]
$CoO \cdot Al_2O_3$, aggregate	25–1000	77–1832	8.5×10^{-6}	Henry[78]
$MnO \cdot Cr_2O_3$, aggregate	25–800	77–1472	9.2	Chesters and Parmelee[50]
$ZnO \cdot Fe_2O_3$, aggregate	25–800	77–1472	9.7	Chesters and Parmelee[50]
$MgO \cdot Fe_2O_3$, aggregate	25–800	77–1472	12.7	Chesters and Parmelee[50]
$FeO \cdot Fe_2O_3$, aggregate	25–800	77–1472	15.5	Chesters and Parmelee[50]
$MnO \cdot Fe_2O_3$, aggregate	25–800	77–1472	11.0	Chesters and Parmelee[50]
90 per cent cordierite, aggregate	20–308	68–586	1.0	Geller and Insley[44]
80 per cent forsterite, aggregate	20–304	68–579	8.3	Geller and Insley[44]
Beryl, ‖ principal axis	20–300	68–572	2.2	Geller and Insley[44]
Beryl, ⊥ principal axis	20–265	68–509	1.0	Geller and Insley[44]
95 per cent zinc orthosilicate	20–350	68–662	1.6	Geller and Insley[44]
Zinc aluminate	20–525	68–977	7.7	Geller and Insley[44]
Celsian, 90 per cent	20–400	68–752	3.4	Geller and Insley[44]
Anorthite, 96 per cent	20–300	68–572	4.3	Geller and Insley[44]
Ceria, aggregate	800	1472	8.6	Henry[78]
$ZrO_2 \cdot Cr_2O_3$, aggregate	800	1472	5.4	Henry[78]
SnO_2, aggregate	800	1472	3.3	Henry[78]
$ZrO_2 \cdot P_2O_3$, aggregate	800	1472	0.5	Henry[78]
Thoria, aggregate	100–500	212–532	9.0	Geller[74]
Beryllia, aggregate	20–1400	60–2562	9.3	Norton
Beryllia, aggregate	800	1472	8.3	White and Shremp[65]
Titania, aggregate	100–500	212–932	7.0	Geller[74]
Chromic oxide, aggregate	100–500	212–932	7.0	Pole *et al.*[75]
Chromic oxide, aggregate	100–500	212–932	12.0	Henry[78]

(about 1800°F) accompanied by a large volume change. However, this transformation may be partially or wholly prevented by stabilizers added to the lattice as discussed in Chap. XII.

5. Reheat Shrinkage of Refractories. To determine the fitness of a particular brick for service, it is often tested for shrinkage under temperature conditions equivalent to those which it would receive in use. This after-shrinkage may be determined by the bar method, as described earlier in this chapter, which has the advantage of giving a continuous record of the shrinkage throughout the range of temperatures, but often it is desirable to make a test on a whole brick.

This is done by first determining the length or volume of the brick by measurement and then subjecting it to a prolonged heating at the desired temperature. After the brick has cooled, it is again measured and the length, volume, and shrinkage determined.

The standard ASTM test for reheat shrinkage is as follows:

STANDARD METHOD OF TEST FOR PERMANENT LINEAR CHANGE AFTER REHEATING OF REFRACTORY BRICK

ASTM Designation: C 113-36[1]

ADOPTED, 1936; REVISED, 1946

This standard of the American Society for Testing Materials is issued under the fixed designation C 113; the final number indicates the year of original adoption or, in the case of revision, the year of last revision.

1. Scope. This method of test covers a procedure for determining the permanent linear change of certain types of refractory materials when heated under prescribed conditions.

2. Apparatus. The apparatus shall consist of a kiln of the down-draft type and of such design as not to permit the flame to impinge directly from the burner upon the test specimens. The kiln atmosphere during the test shall be kept as oxidizing as is practicable.

3. Test Specimens. *a.* The test specimens shall consist of three standard 9-in. brick (9 × 4½ × 2½ in.) or three pieces of these dimensions cut out of larger shapes.

b. Each test specimen shall be labeled with ceramic paint and carefully measured for length before and after reheating. The measurements shall be made by the use of a firm joint caliper and a steel rule. The calipering shall be done at the center of each end, and the dimension shall be measured to the nearest 0.02 in., or 0.5 mm.

4. Location of Test Specimens in Kiln. The test specimen shall be placed in the kiln so that each will rest on a 9 by 2½-in. face and only one course high. Each specimen shall be placed upon the 9 by 2½-in. face of a supporting brick

[1] ASTM Standards are subject to revision. The Society's headquarters, in Philadelphia, may be consulted for the latest information.

TABLE 87. CHANGE IN LINEAR DIMENSIONS ON REHEATING*

Brick	Per cent of change after heating	
	5 hr. at 1400°C. (2557°F.)†	5 hr. at 1500°C. (2732°F.)
Pennsylvania.....	0.7	
	−0.6	
	0.1	
	0.3	
	1.3	
	0.1	
	−1.6	
	0.8	**2.1**
	0.3	
	0.2	
	0.1	
	−1.8	
	−0.2	
	1.1	
	1.4	2.6
Missouri.....	−0.3	−0 4
	−0.8	−0.7
	0.3	
	0.8	
	−0.2	
	0.1	
	−0.1	
	−0.2	
	−0.2	
	−0.1	
	−0.4	
Kentucky.....	1.7	4.5
California.....	0.0	
	−0.2	
	0.0	
Maryland.....	0.2	
	0.3	
	0.3	
	0.0	
	0.3	
Colorado.....	−0.7	−1.2
New Jersey.....	0.1	−0.8
New Jersey.....	0.2	−1.7

* Heat Measurements Laboratory, Massachusetts Institute of Technology.
† Negative sign indicates shrinkage.

which shall be from the same lot as the test specimen or at least of equal refractoriness. There shall be placed between the test specimen and the supporting brick a layer of calcined diaspore, kyanite, or fused alumina ground to pass a No. 20 (840 μ) ASTM sieve (equivalent to mesh No. 20 of the Tyler standard series). Each specimen shall be placed so as to be not closer than 1½ in. from other test specimens or the furnace wall.

5. Temperature Measurement. *a.* The temperature within the kiln shall be measured by means of a platinum platinum-rhodium thermocouple and a potentiometer, preferably a recording potentiometer. The hot junction of the couple shall be placed so as to register the temperature of the test specimens. The kiln shall be of uniform temperature over the hearth and shall be checked from time to time by means of cones and they shall not show a difference of more than one cone. At 2560°F (1405°C), the thermocouple should be withdrawn and an optical pyrometer shall be used. The sighting shall be directed upon one of the test specimens.

b. During the constant temperature period of the test, the temperature as measured by the thermocouple shall not be allowed to vary by more than ±10°C and, in the case of the optical pyrometer, ±15°C. Temperature readings shall be made at intervals not greater than 15 min.

6. Test Temperature Schedules. The kiln shall be operated so as to conform to the temperature schedule specified for the particular test to be conducted. Heating schedules for various classes of refractories are shown in the following table:

HEATING SCHEDULE FOR REHEAT TEST OF VARIOUS TYPES OF REFRACTORIES

Elapsed time from start of heating, hr.	Temperature of test specimen, °C.			
	Schedule A	Schedule B	Schedule C	Schedule D
1	Between 700–800	Between 900–1000	Between 900–1000	Between 825 and 925
2	Between 1075–1125	Between 1275–1325	Between 1275–1325	Between 1225 and 1275
3	1200 ± 10 maintained for 5 hr.	1400 ± 10 maintained for 5 hr.	Between 1450–1500	1350 ± 10 maintained for 5 hr.
4			Between 1550–1575	
5			1600 ± 15 maintained for 5 hr.	

7. Cooling. After completion of the heating period the test specimens shall be allowed to cool in the closed kiln for a period of at least 10 hr.

8. Calculation. The test specimens shall be remeasured after rubbing the ends with an abrasive block to remove small blisters. The percentage linear change based upon the original length shall be calculated and reported as the average value of the three test specimens.

In Table 87 are given some values for typical fireclay bricks under the standard test conditions. A few values are also given at 1500°C (2732°F).

It is interesting to notice that this test indicates an expansion as often as a shrinkage. This reheat volume increase is known both as "secondary expansion" and "afterexpansion." At the higher temperature, the shrinkage or expansion is usually increased; but in some cases, there is little change; and in others, an actual reversal in sign occurs.

Another test that determines the aftershrinkage of a brick is the simulative service test used by the U.S. Navy. According to the description by Rogers,[31] it consists in building up two walls of a furnace, one of the brick to be tested and the other of a standard brick. The furnace is then run for 24 hr at a temperature of 1590°C (about 2900°F) and again at 1650°C (about 3000°F), with an examination of the walls between the tests. An examination of the wall after it is cooled will indicate by the width of the open joints the approximate shrinkage of the bricks. The photographs in Figs. 298 and 299 show typical walls. This test is, of course, not quantitative, but it does more or less correspond to actual service conditions. It is believed that a wall which shrinks a small amount at each joint is better than a wall which concentrates its shrinkage into a few large cracks. It should also be realized that a wall may have a considerable amount of open joints when cool and yet be substantially tight when at a high temperature.

As previously mentioned, bricks may show either an expansion or a shrinkage when heated to the temperatures of service. In general, bricks are not burned so high in the process of manufacture as the temperature of service; consequently, with the usual type of clay, the brick will decrease in volume at service temperatures. This is undesirable, especially in crowns and arches, because the open joints resulting give corners for spalling and slag erosion to start. The open cracks also concentrate the load in the arch on a relatively small area of the block, which greatly decreases the stability of the structure. A slight expansion is not particularly harmful if the wall or arch is properly designed.

Theory of Secondary Expansion. There are three phenomena that may produce an increase in volume of ware subjected to the reheat test. They are

1. Overfiring, *i.e.*, development of a vesicular structure, or bloating.
2. Opening of the laminations of the clay.
3. Transformations or reactions in the crystalline phases during the firing, yielding products of lower true density than the reactants.

In general, these phenomena take place in certain definite temperature ranges. When the temperature at which a brick is first fired is below this range, the brick may expand if subjected to a reheat temperature in the expansion range. When the temperature of the initial firing is in the expansion range, the ware may shrink, expand, or stay constant in volume in the reheat test, depending upon the time and the atmosphere of firing.

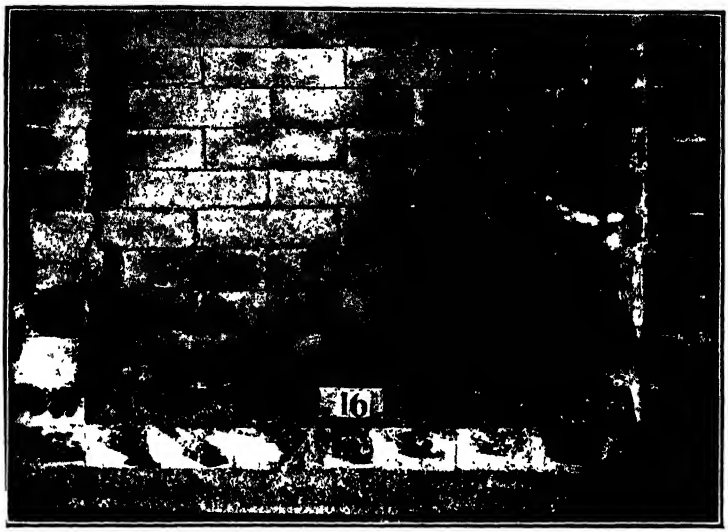


FIG. 298. Simulative service test, after a 1650°C (3000°F) heat. Bricks in fair condition.

The reactions that take place to cause overfiring have been discussed in Chap. VIII. Overfiring occurs in certain clays, especially plastic clays, and it is probable that the decomposition of some materials, perhaps sulfides and sulfates, is inhibited so gases are not given off until a temperature

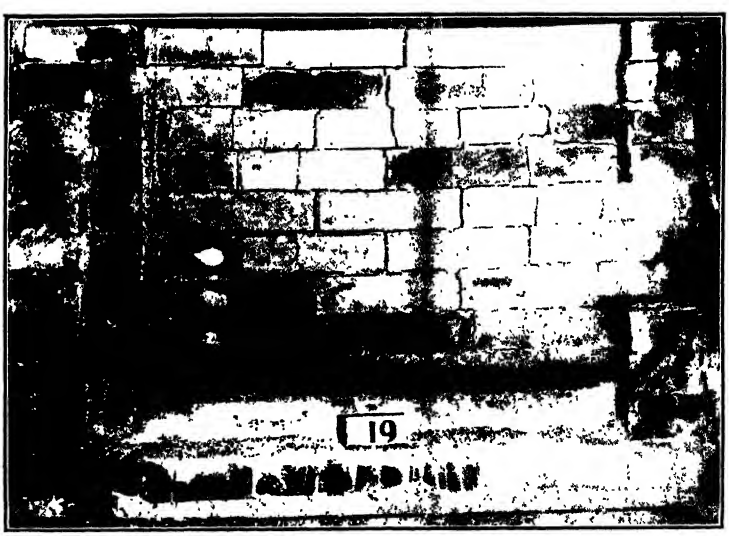


FIG. 299. Simulative service test, after a 1650°C (3000°F) heat. Bricks in poor condition.

CHAPTER XVIII

HEAT TRANSMISSION BY REFRACTORIES

1. Introduction. In certain parts of a furnace, such as the walls or roof, a minimum transmission of heat to the outside is desired; hence, a refractory with a low thermal conductivity would be necessary for these conditions. On the other hand, such parts as muffles or underfired hearths require a refractory with a high conductivity value. It will therefore be seen that the furnace designer must have accurate data on the thermal conductivity of his refractories before he can intelligently select his materials or predict the performance of his furnace.

2. Laws of Heat Conduction. *Definitions and Units.* The following symbols have been generally adopted in reference to heat flow:

q = the quantity of heat conducted in Btu per hr
t_0 = the initial temperature in variable flow
t_1 = the temperature of the hotter surface, °F
t_n = the temperature of the cooler surface, °F
L = the thickness of the wall, in. (or length of heat path)
k = the conductivity of the material, Btu/(hr)(ft²)(in.)(°F)
A = the area of the section normal to the flow, sq ft
x = the distance from the hotter surface, in.
h^2 = the diffusivity = k/pc
ρ = bulk density, lb per cu ft
c = specific heat
τ = time, hr

Table 88[70] gives factors to convert the common units of heat flow into others. Throughout the chapter, engineering units will be used, except for the values of single crystals and glasses.

Steady Flow. For conditions of steady flow, the amount of heat passing through a wall is expressed by

$$q = \frac{kA(t_1 - t_n)}{L}$$

or if we consider a unit area of 1 sq ft, then

$$q = \frac{t_1 - t_n}{L/k} \tag{1}$$

for a simple wall.

TABLE 88. CONVERSION FACTORS*
Units of Conductance of Energy: Thermal and Electrical

	G.-cal. · sec.$^{-1}$ · cm.$^{-2}$ · cm. · °C^{-1}	Kg.-cal. · hr.$^{-1}$ · cm.$^{-2}$ · cm. · °C^{-1}	Watt · cm.$^{-2}$ · cm. · °C^{-1}	Watt · in.$^{-2}$ · in. · °C^{-1}	Kw. · ft.$^{-2}$ · in. · °C^{-1}	Kw. · ft.$^{-2}$ · in. · °F^{-1}	B.t.u. · hr.$^{-1}$ · in.$^{-2}$ · in. · °F^{-1}	B.t.u. · hr.$^{-1}$ · ft.$^{-2}$ · in. · °F^{-1}	B.t.u. · hr.$^{-1}$ · ft.$^{-2}$ · ft. · °F^{-1}	B.t.u. · hr.$^{-1}$ · ft.$^{-2}$ · in. · °C^{-1}
1 g.-cal. · sec.$^{-1}$ · cm.$^{-2}$ · cm. · °C^{-1}	1	3.600	4 186	10.63	1.531	0 8506	20.16	2903	241.9	5225.8
1 kg.-cal. · hr.$^{-1}$ · cm.$^{-2}$ · cm. · °C^{-1}	0.2778	1	1 163	2 953	0 4253	0 2363	5 600	806.4	67.20	1452
1 watt · cm.$^{-2}$ · cm. · °C^{-1}	0.2389	0 8600	1	2 540	0 3658	0 2032	4 816	693 5	57 79	1248
1 watt · in.$^{-2}$ · in. · °C^{-1}	0.09405	0 3386	0.3937	1	0.1440	0.08000	1.896	273 0	22.75	491.5
1 kw. · ft.$^{-2}$ · in. · °C^{-1}	0.6531	2.351	2.734	6.944	1	0 5556	13 17	1896	158 0	3413
1 kw. · ft.$^{-2}$ · in. · °F^{-1}	1.176	4 232	4 921	12 50	1 800	1	23 70	3413	284 4	6143
1 B.t.u. · hr.$^{-1}$ · in.$^{-2}$ · in. · °F^{-1}	0.04960	0 1786	0 2076	0 5274	0 07595	0 04219	1	144 0	12 00	259 2
1 B.t.u. hr.$^{-1}$ · ft.$^{-2}$ · in. · °F^{-1}	$3\ 445 \times 10^{-4}$	0 001240	0 001442	0 003663	$5\ 274 \times 10^{-4}$	$2\ 930 \times 10^{-4}$	0 006944	1	0 08333	1.800
1 B.t.u. · hr.$^{-1}$ · ft.$^{-2}$ · ft. · °F^{-1}	0 004134	0 01488	0 01730	0 04395	0 006329	0 003516	0 08333	12 00	1	21.60
1 B.t.u. · hr.$^{-1}$ · ft.$^{-2}$ · in. · °C^{-1}	$1\ 914 \times 10^{-4}$	$6\ 889 \times 10^{-4}$	$8\ 011 \times 10^{-4}$	0 002035	$2\ 930 \times 10^{-4}$	1 628	0 003858	0.5556	0 04630	1

* Based on International Critical Tables; mean values used for kg.-cal. and B.t.u.; from White, American Ceramic Society.[70]

In a composite wall made up of several layers, the value of q is obviously the same for each layer under steady conditions; therefore

$$q = \frac{t_1 - t_n}{(L_1/k_1) + (L_2/k_2) + \cdots (L_n/k_n)} \tag{2}$$

where $L_1, L_2, \ldots L_n$ and $k_1, k_2, \ldots k_n$ refer to the properties of each layer, respectively.

Since the temperature drop across each layer is equal to the heat flow times the actual resistance of the respective layers, we may say

$$t_1 - t_2 = q \frac{L_1}{k_1} \tag{3}$$

$$t_2 - t_3 = q \frac{L_2}{k_2} \cdots \tag{4}$$

From these temperature drops, the interface temperatures can be computed. It should also be remembered that the value of q entering the hot face and leaving the cool face is equal to the q of each layer.

Variable Flow. In practice, many cases of unsteady heat flow occur, as in batch-type furnaces. In a simple case, suppose that a wall is suddenly heated from t_0 to t_1 on one face. The temperature at a point x distant from the face is given by Fourier's equation.

$$t = \frac{2t_0}{\sqrt{\pi}} \int^{\infty} \frac{x}{2h\sqrt{\tau}} e^{-\beta^2} \, d\beta \tag{5}$$

where β = a variable of integration.

It will be seen that the penetration of heat will depend on time and the value of diffusivity. An infinite time is required theoretically to reach equilibrium, and practical equilibrium requires many hours in thick walls. In Fig. 300 are shown curves of temperature rise of the cool face in refractory walls of various thicknesses that have suddenly been heated on one face. When the hot face is not brought up suddenly but at a definite schedule, the calculations are difficult. They may be approximated, however, by adding an imaginary layer to the hot face of the wall, as suggested by Ingersoll and Zobel,[2] or the Schmidt method may be used as illustrated by Trinks.[16]

3. Theory of Heat Transfer through a Porous Body. Since most refractories are more or less porous, it is of interest to see how this porosity influences the transfer rate.

Conduction. Some of the heat is conducted through the body by virtue of the close contact of the particles making up the structure. This conduction will be decreased as the porosity increases.

Convection. If the pores are filled with air or combustion gases, as would usually be the case, some heat is transferred by convection currents in the pore itself. This transfer is so small as to be negligible for the usual size of pores.

Radiation. A considerable portion of the heat flow at high temperatures may be due to direct radiation across the pores. For a given amount of porosity, the large pores will transfer more heat by radiation.

The radiant heat transferred is also proportional to the emissivity of the refractory surface. These total emission coefficients are not accurately

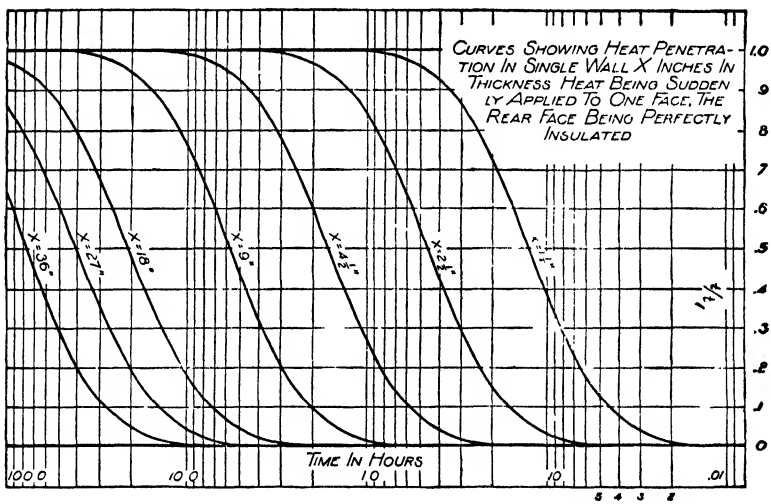


FIG. 300. Heat-penetration curves; t_1 = temperature of heated face, t = temperature of rear face, x = wall thickness.

known at high temperatures, but some figures by Heilman[52] indicate that a black brick such as chrome has a value of 0.97 whereas a white refractory like a kaolin brick has a value as low as 0.3. During 1948, J. M. Brownlow, working under Professor Wilkes in the Heat Measurements Laboratory of the Massachusetts Institute of Technology, developed an ingenious method of measuring total emission coefficients. This consisted of revolving a cylinder of refractory in a globar-heated furnace, with a narrow portion of the cylinder exposed to the open. The true temperature of the cylinder, kept uniform by rapid turning, was measured by a platinum thermocouple on the axis, and the apparent surface temperature at the exposed point, with a radiation pyrometer. From these two readings the coefficient could be computed readily.

The results on a few materials are shown in Fig. 301. The fused magnesia, alumina, and zirconia specimens were made by the Norton Company

of their regular material. The kaolin insulating brick was a Babcock and Wilcox K-28, and the dense kaolin was this same specimen coated with a kaolin cement. Most of the specimens have values quite close together except for the silicon carbide, which averages 0.9. The influence of surface roughness is very evident in the kaolin materials, as the porous structure

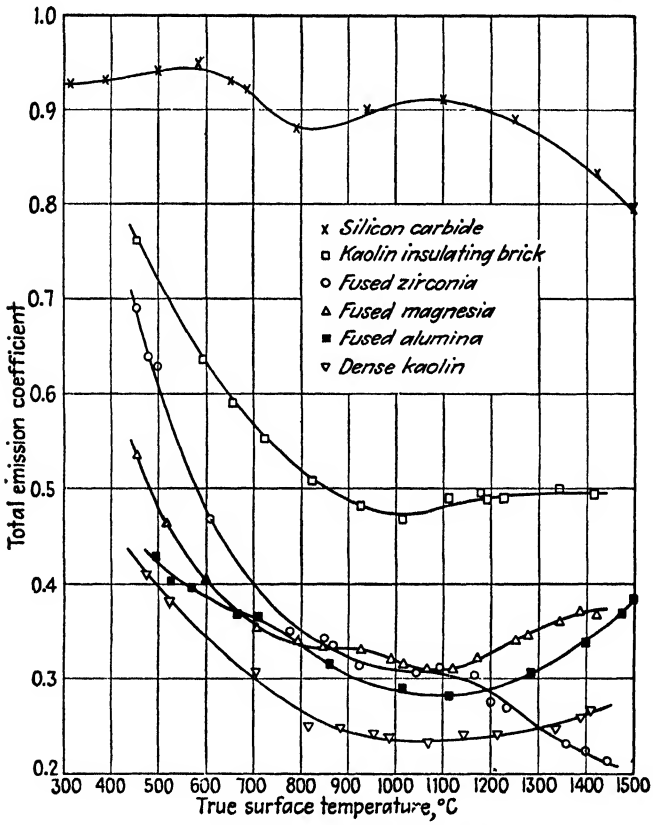


FIG. 301. Emission coefficients of refractories.

has twice the value of the dense one. Further work should be carried out in this field.

There is an excellent opportunity for anyone interested in the field of high-temperature insulators to do some valuable work by correlating the theoretical and measured values of k for materials with various types of porosity and emissivity. The work of Waddams[76] gives some interesting results at medium temperatures.

4. Measurement of Thermal Conductivity. *The High-temperature Calorimeter Method.* Most of the high-temperature tests on refractories

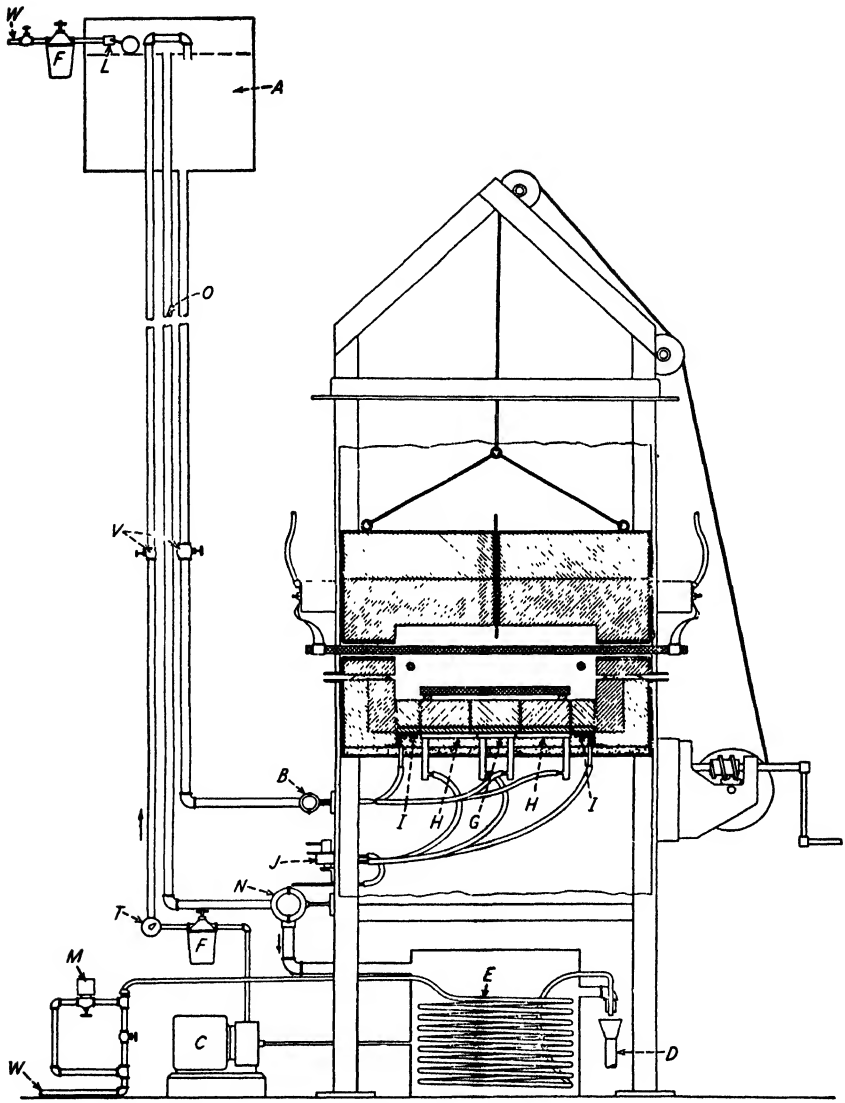


FIG. 302. Diagram showing essential parts of thermal conductivity apparatus.

A—Constant head water supply.
B—Inlet manifold and thermometer.
C—Circulating pump.
D—To drain.
E—Cooling coil.
F—Water filter.
G—Center calorimeter.
H—Inner guard calorimeters.
I—Outer guard calorimeters.
J—Microregulating valves.
L—Water level valve.
M—Magnetic control valve.
N—Outlet manifold.
O—Overflow pipe.
T—Thermostat (Controls M).
V—Valves.
W—Water inlet.

for thermal conductivity have been made by setting up a uniform parallel flow of heat normal to the faces of a slab. The quantity of heat flowing is measured by a water calorimeter on the cold face of the specimen, and the temperature gradient by the thickness and hot- and cold-face temperatures.

The establishment of a uniform flow is by no means easy, and only by careful guarding can this be accomplished. Also the temperatures on the isothermal planes must be read with great care. At the same time, an equilibrium flow must be established by a constant hot-face temperature

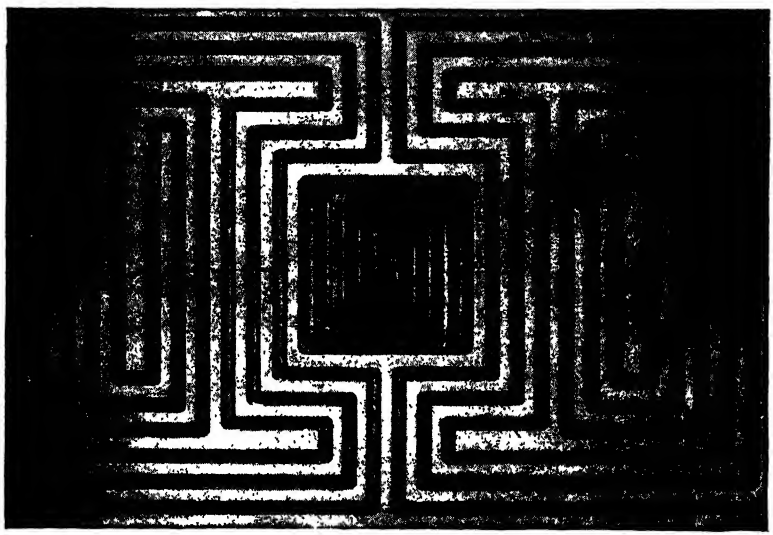


FIG. 303. Water passages in the calorimeter and guard ring.

for a long time interval. Perhaps no other physical measurement is beset with so many pitfalls. The papers by Norton[73] and Patton and Norton[74] give an excellent discussion of these errors and their correction.

This method can best be explained by an example of a high-temperature plate tester originally suggested by Wilkes but later constructed in many laboratories with minor changes. The following description applies to an apparatus recently constructed in the refractories laboratory of the Babcock and Wilcox Company[73] and later made ASTM Standard Method C 201-47.

A drawing of this apparatus is shown in Fig. 302. In Fig. 303 is shown the arrangement of water passages in the calorimeter and guard ring.

Special features are the constant-temperature water source, the temperature control of the furnace to maintain the temperature for the 24-hr run within $\pm 2°F$ (about 1°C), and the flow passages in the calorimeter.

The method of making a test will be made clear by the following example in Table 89 of a run made on an insulating firebrick.

TABLE 89. TYPICAL THERMAL-CONDUCTIVITY RUN

Time	Difference between guard and calorimeter, M.V.	Difference between inlet and outlet of calorimeter, M.V.	Hot face, M.V.	Center, M.V.	Cold face, M.V.	Water flow, per cc. min.
9:00	0.002	0.030	4.62	13.73	1.70	
10:00	0.000	0.028	4.83	13 93	1.79	360
10:40	0 000	0.030	4.72	13.77	1.70	358
11:00	0.000	0.029	4.76	13.79	1.72	361
11:30	0 000	0.029	4.65	13 76	1.68	370
12:34	0.000	0.029	4.62	13.67	1.68	367
1:45	0.000	0.027	4 63	13 64	1.67	360
2:15	0 000	0.028	4.63	13 65	1.68	
3:15	0.000	0.027	4.63	13 66	1.67	360
	= 0°F.	= 0.24°C.	= 995°F.	= 630°F.	= 105°F.	

$$q = 0.24 \times 3.83 \times 360 = 332 \text{ B.t.u. per hr.}$$

$$\frac{332 \times 1.25}{630 - 105} \quad \frac{414}{525} = 0.79 = k \text{ at } 368°\text{F.}$$

$$\frac{332 \times 2.5}{995 - 105} = \frac{830}{890} = 0.93 = k \text{ at } 550°\text{F.}$$

$$\frac{332 \times 1.25}{995 - 630} = \frac{414}{365} \quad 1.13 = k \text{ at } 812°\text{F.}$$

Thermal conductivity is measured in other ways; *e.g.*, a cylindrical specimen is sometimes convenient as shown in Fig. 304, which represents a pipe cover tester. In this way, edge losses are minimized, because the area of

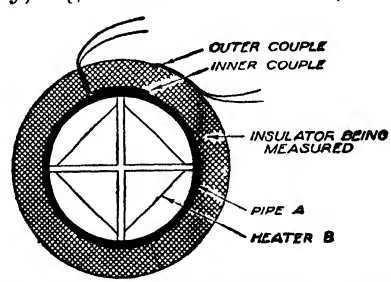


FIG. 304. Pipe tester for measuring thermal conductivity.

the ends is small compared with the outside area, but it is often difficult to obtain standard refractories of the proper shape. The cylindrical method, however, has been used by Holler[59] and others for high-temperature tests.

The Northrup method consists in passing a uniform, linear flow of heat through two layers of refractory in contact. If the temperature drop is known through each layer and the value of k known for one material, the conductivity of the other layer can be readily determined, as the value of q must be the same for both. The following relation holds:

$$\frac{\text{Temperature drop in specimen } A}{\text{Temperature drop in specimen } B} = \frac{k_B}{k_A}$$

Harmonic-flow Method. A somewhat different method has been used to determine the thermal conductivity by making use of Fourier's equation for nonuniform heat flow. If we consider Eq. (5) in this chapter, it will be noticed that the value of h^2, the diffusivity, can be determined by studying the temperature changes in a given material. From the value of h, the thermal conductivity can be computed if the density and specific heat are known, properties that are not difficult to measure. This method has been carried out practically by applying to one surface of the test material a temperature varying harmonically. The temperature is then recorded inside the solid at several distances from the surface; and from these values, h can be computed. It will be noticed that this method does not necessitate a measurement of the quantity of heat flowing. On the other hand, the same difficulties are encountered in ensuring a linear flow of heat as in the other methods, and the problem of providing a sinusoidal heat supply at high temperatures is a serious one. Another method of measurement of this type consists in computing the diffusivity by measuring the temperature change on the axis of a cylinder, the outside temperature of which is suddenly changed by quenching. This may be found quite convenient and precise for small specimens such as pure oxides.

5. Thermal-conductivity Values for Refractories and Insulators. *Crystals and Glasses.* The available data for crystals and glasses are very meager at low temperatures and nonexistent at high temperatures. A few values are shown in Table 90 to bring out three important facts: (1) The thermal conductivity for some crystals decreases with increasing temperature, probably reaching a minimum and then increasing again, whereas for glasses it always increases. (2) The k value for a crystal with an orderly arrangement of atoms is greater than that for a corresponding glass as shown for the case of silica. (3) The conductivity of nonisotropic crystals varies with the direction of heat flow, being a maximum along one principal axis and a minimum along another. The ratio of the maximum and minimum k for a number of crystals is shown in the last column of Table 90.

At present, there are insufficient data to formulate a relation between atomic structure and thermal conductivity with any certainty. However,

TABLE 90. THERMAL CONDUCTIVITY OF SINGLE CRYSTALS AND GLASS

Material	Mean thermal conductivity, cgs units, at a mean temperature of							Ratio of minimum to maximum k at 200°C	Reference
	0°C	100°C	200°C	300°C	400°C	500°C	600°C		
Quartz, ∥ C-axis		0.021	0.016	0.014	0.013	0.012			Knapp[75]
Quartz, ⊥ C-axis	0.027	0.019	0.015	0.012	0.010				Birch and Clark[72]
Quartz, ∥ C-axis		0.009	0.009	0.009	0.010	0.011		0.57	Knapp[75]
Quartz, ⊥ C-axis	0.016	0.012	0.010	0.008	0.007				Birch and Clark[72]
Quartz, ∥ C-axis	0.032	0.021							Eucken[42]
Quartz, ⊥ C-axis	0.017	0.010							Eucken[42]
Fused silica		0.004	0.004	0.005	0.006	0.008	0.011		Knapp[75]
Soda-lime glass		0.003	0.004	0.005	0.006				Knapp[75]
Pyrex glass		0.003	0.004	0.005	0.006	0.007			Knapp[75]
Corundum, ∥ C-axis		0.014	0.015	0.016	0.016	0.017			Knapp[75]
Corundum, ⊥ C-axis		0.009	0.010	0.010	0.012	0.015		0.67	Knapp[75]
Synth. sapphire, C-axis		0.008	0.009	0.010	0.012	0.015			Knapp[75]
Beryl, ∥ C-axis		0.007	0.008	0.009	0.011	0.012			Knapp[75]
Beryl, ⊥ C-axis		0.006	0.007	0.008	0.010	0.011		0.88	Knapp[75]
Tourmaline, ∥ C-axis		0.004	0.005	0.006	0.007	0.008			Knapp[75]
Tourmaline, ⊥ C-axis		0.005	0.006	0.007	0.008	0.009		0.83	Knapp[75]
Lithium fluoride		0.006	0.008	0.100	0.012	0.014			Knapp[75]
Topaz, ∥ C-axis		0.012	0.012	0.012	0.013	0.017			Knapp[75]
Topaz, ∥ B-axis		0.011	0.011	0.011	0.012	0.015		0.92	Knapp[75]
Topaz, ∥ A-axis		0.010	0.010	0.010	0.011	0.014		0.83	Knapp[75]
Topaz, average	0.056								Eucken[42]
Zircon, ⊥ C-axis		0.006	0.009	0.010	0.012	0.013			Knapp[75]
Periclase		0.013	0.016	0.018	0.021	0.022			Knapp[75]
Dense SiC (not a single crystal)		0.021	0.023	0.022	0.022	0.021			Knapp[75]
Mullite fibers, ∥ C-axis		0.009	0.009	0.010	0.011	0.013			Knapp[75]
Mullite fibers, ⊥ C-axis		0.006	0.006	0.007	0.008	0.009		0.67	Knapp[75]

the following equation proposed by Compton[3] seems best to fit the experimental results.

$$k = bn^2\, dR\, v\, \frac{2 - cT^{1/2} \cdot e^{-Bv/2T}}{c^2 T}$$

where $b = 1$

n^2 = the number of atoms per unit area of the plane normal to the heat flow

d = the distance between neighboring atoms

v = the natural frequency of the atoms

c = determined by the conductivity at a given temperature

B = a universal constant

The field of research connecting thermal conductivity with atomic structure is almost virgin territory and offers excellent opportunity for further work, especially in developing a precise method of measuring k up to high temperatures on very small specimens.

Heavy Refractories. The commercial refractory consists of crystalline material alone or with a glass bond. Usually the crystals are small and randomly oriented. We should expect, from the preceding data, that the value of k would be higher for those refractories consisting of well-bonded crystals with the glass phase eliminated. For example, the recrystallized silicon carbide contains very little glass and has a high conductivity value. A great deal more research is needed on the conductivity of refractories made of crystals, glass, and air in varying proportions. Some values of thermal conductivity for heavy refractories are shown in Table 91. Owing to experimental difficulties, the values for heavy refractories cannot be depended on so closely as those for insulators.

Insulators. Insulators are composed of a more or less refractory skeleton having a large proportion of pores. The basic material may be mag-

TABLE 91. HEAVY REFRACTORY BRICK
Mean Thermal Conductivity* at a Mean Temperature, °F

Type of Brick	Apparent porosity, per cent	400	800	1200	1600	2000	2400	Reference
Alumina, fused	21 3	18 5	21.7	24 2	26 7	28 4	30 0	Norton[30]
Carbon					18.5	22 0		Powell and Schofield[71]
Chrome	30 5	10 0	10 8	11 3	11 6	11 8	12 0	Norton[30]
Fireclay	15 2	8.1	8 4	10 1	10 8	11.4	12 0	Wilkes[49]
	18 4	7 3	8.7	9.8	10 6	11 6	11 8	Norton[30]
	26 7	7 0	7.8	8 7	9 3	10 2	10.5	Norton[30]
Super-duty fireclay		7 5	8.4	9 0	9 5	9 8		Patton and Norton[74]
Graphite		730	500	400	310	220		Powell and Schofield[71]
Kaolin	10 8	13.5	15.0	16 3	18 0	18.8	19 7	Norton[30]
	23 2	10 0	10 9	11.9	12.8	13 4	13 8	Norton[30]
	49 1	3.0	4.4	5 2	6 1	6 7	7 1	Norton[30]
Magnesite	29	25 8	22 0	18 2	15 7	13 7	12 6	Wilkes[49]
	31.6	39 2	35 2	29 0	26.7	25 6	25 0	Norton[30]
Silicon carbide clay	28.3	26	26	29	34	38	50	Wilkes[49]
Silicon carbide clay 5 per cent	16.2		17.5	155	135	118		Holler[59]
Silicon carbide clay 20 per cent	21 0		70	61	58	57		Holler[59]
Silicon carbide, recrystallized	34 4	210	175	150	115	95	81	Wilkes[49]
	35 3		143	126	105	93	80	Norton[30]
Silica	28 0	6.5	8.5	10.5	12.4	14.0	15.7	Austin and Pierce[56]
		7.5	8.0	9 0	10.0	10 9		Patton and Norton[74]
	30 4	8.1	10.0	11 8	13 0	14 2	15.3	Norton[30]
Spinel	36.3	10 4	11.6	12 5	13 3	14.0	14.6	Norton[30]
99 + per cent, fused alumina	21		27	20	18	17		Whittemore[80]
	36		19	16	14	12		Whittemore[80]
	47		13	11	9	8		Whittemore[80]
	57		7	6	6	6		Whittemore[80]
96–99 per cent fused MgO	19		28	23	20	17		Whittemore[80]
98–99 per cent ZrO_2 fused + CaO stabilized	26		5	5	5	6		Whittemore[80]
	44		3	3	4	5		Whittemore[80]
Zirconia (Baddeleyite)	29.5	10.4	11.3	12.2	13.0	13.7	14.3	Norton[30]

* k expressed as Btu per hr per sq ft per in. per °F.

TABLE 92. THERMAL CONDUCTIVITY OF INSULATING MATERIALS

Type of insulation	Linear shrinkage—5-hr. reheat, per cent at °F.	Density, lb. per cu. ft.	Mean thermal conductivity* at a mean temperature of						
			200°F.	400°F.	800°F.	1200°F.	1600°F.	2000°F.	2400°F.
Insulating firebrick:									
Kaolin base	1.00 at 2900	55			2.9	3.3	3.9	4.5	5.2
Kaolin base	1.00 at 2800	44			2.1	2.8	3.3	3.8	4.4
Fireclay base	3.10 at 2600	48		2.5	2.8	3.2	3.7		
Kaolin base	0.10 at 2300	26		0.8	1.0	1.3	1.5		
Insulating brick:									
Raw diatomaceous earth base	1.00 at 1400	33	0.7	0.8	0.9	1.0			
Calcined diatomaceous earth base	2.80 at 2300	43			1.4	1.6	2.0		
High-temperature block insulation:									
Diatomaceous earth base	3.10 at 1900	23	0.58	0.62	0.70	0.80			
Vermiculite base	0.75 at 1600	18.5	0 55	0.67	0.80	0.95			
Mineral wool base	1.69 at 1600	22	0 42	0.56	0.84				
Kaolin base		19	0.58	0.67	0.91	1 21			
Insulating blankets:									
Mineral-wool base	1000	8–12	0.38	0.52	0.78				
Mineral-wool base	800	8–12	0 35	0.51					
Glass-wool base	1000	3	0.31	0.36	0.57				
Plastic insulating cements:									
Diatomaceous base	1900	40	0.65	0.72	0.82	1.00			
Mineral-wool base	1200	24	0.67	0.75	0 93				
Vermiculite base	1500	15	0.75	0.83	1 10				
Asbestos base	1200	17	0.80	0.93	1 25				
85 per cent magnesia	600	15	0.49	0.55					

* k expressed as Btu per hr per ft per in per °F

nesium carbonate, asbestos, silica, clay, or glass fibers. The values of k for a number of typical materials are shown in Table 92. For data on any specific product, it is necessary to get in touch with the manufacturer or make an individual test of the material.

It will be noted that in general, the lighter the insulator the lower will be the value of k at low temperatures. There is a lower limit, however, as mineral wool, for example, below 5 lb per cu ft density shows an increasing value of k. In general, material with the smallest pores has the slowest increase in conductivity with increasing temperature; but here again, much research is needed to develop a general theory of heat conduction in porous materials, although this has been considered by some writers.[42]

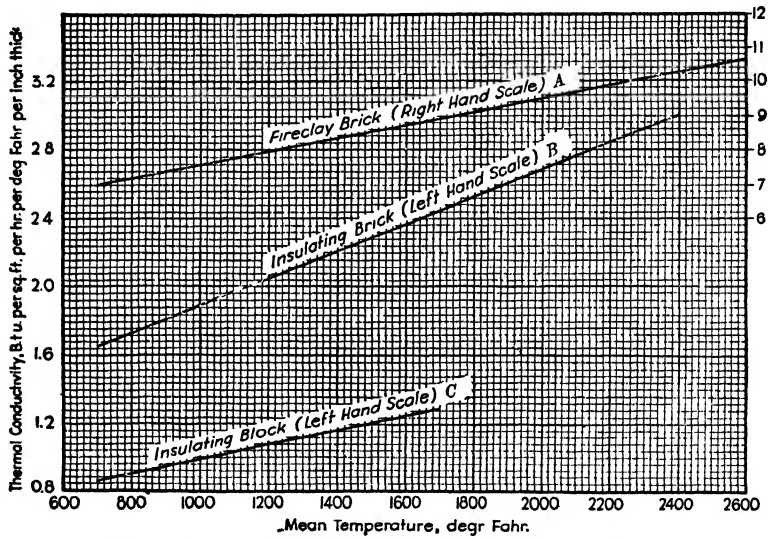


FIG. 305. Average curves of thermal conductivity used in calculations. (*From R. H. Heilman, ASTM Committee C-8 on Refractories.*)

6. Flow of Heat through Walls under Steady Conditions. *Computation of Heat Flow in a Simple Wall.* The flow of heat through simple walls is dependent on the thermal conductivity at the mean wall temperature and the temperature difference between the hot and cold face. Also it should be remembered that the quantity of heat passing through the wall must be equal to the heat leaving the wall. The latter is also dependent on the cold-face temperature and the velocity of the air outside the wall.

The calculation of the heat flow will be made clearer by a specific example. Assume a 9-in. refractory wall heated on the hot side to 2200°F. The outside air is 80°F and not moving. The values of k for this particular refractory are given by curve A in Fig. 305. The quantity

of heat lost from the outside of the wall, q_{rc}, is given by Heilman's curve in Fig. 306. We may write from Eq. (1)

$$q = \frac{t_1 - t_n}{L/k} = \frac{2200 - t_n}{9/k} = q_{rc}$$

but as k varies with $(t_1 - t_n)/2$ and q_{rc} varies with t_n, the equation cannot be solved directly. Therefore, we must assume a mean temperature and an

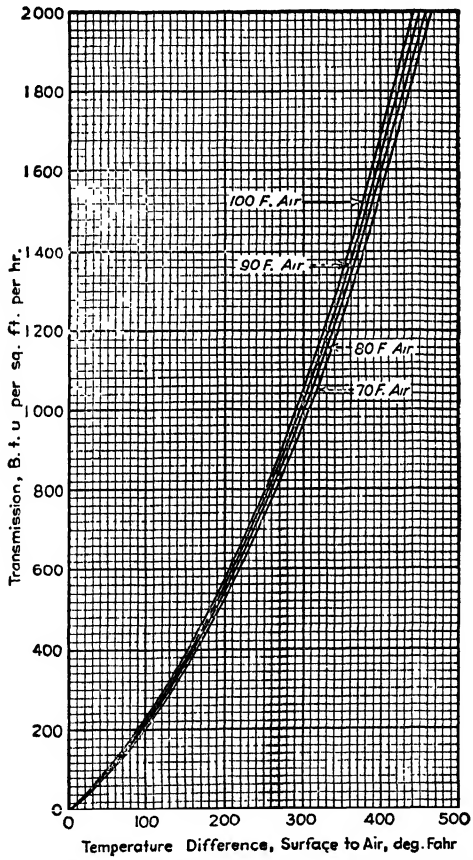


FIG. 306. Heat transmission from a vertical surface. (*From R. H. Heilman, ASTM Committee C-8 Refractories.*)

outside temperature. If q and q_{rc} are not equal, another and closer assumption of values is made until the required precision is reached. Assume $t_n = 300°\text{F}$ and $k = 8.1$, then

$$q = \frac{2200 - 300}{9/8.1} = 1710 \qquad q_{rc} = 620 \text{ from curve}$$

The cold face has been taken too low, so 500 will be taken for the next trial.

$$q = \frac{2200 - 500}{9/8.1} = 1720 \qquad q_{rc} = 1530 \text{ from curve}$$

This gives a mean temperature of 1350°F; hence, a more precise value of k from the curve is 8.2. Choosing a lower cold-face temperature of 480°F gives

$$q = \frac{2200 - 480}{9/8.2} = 1570 \qquad q_{rc} = 1590$$

which is sufficiently close.

Computation of Heat Flow in a Compound Wall. In this case, the value of q is the same for each layer of the wall of unit area and equal to the heat leaving the cold face. As another example, a 9-in. firebrick wall with a 2400°F hot face is backed up with 4.5 in. of insulating brick and 2 in. of insulating block. The air conditions are the same as before. From Eq. (2)

$$q = \frac{2400 - t_n}{(9/k_1) + (4.5/k_2) + 2/k_3} = q_{rc}$$

As a first trial, assume $t_n = 280$°F and k_1, k_2, and k_3 as 9.5, 2.0, and 0.9, respectively, from Fig. 305. Then

$$q = \frac{2400 - 280}{(9/9.5) + (4.5/2.0) + (2/0.9)} = \frac{2120}{0.95 + 2.25 + 2.23} = 390$$

$$q_{rc} = 545 \text{ from curve}$$

Next assume $t_n = 245$, then

$$q = 398 \qquad q_{rc} = 417$$

which is sufficiently close for a first approximation.
Now from Eq. (3)

$$\begin{aligned} t_1 - t_2 &= 398 \times 0.95 = 375 \\ t_2 - t_3 &= 398 \times 2.25 = 895 \\ t_3 - t_n &= 398 \times 2.23 = 890 \\ t_1 - t_n &= \qquad\qquad 2160 \end{aligned}$$

The interface temperatures will be 2025 and 1130°F; the mean temperatures of each layer will be 2212, 1577, and 685°F. Now go back to the conductivity curves and select more precise values of k, which will be, respectively, 9.90, 2.35, and 0.85. The heat flow is now worked out again, with $t_n = 245$.

$$q = \frac{2400 - 245}{(9/9.9) + (4.5/2.35) + (2/0.85)} = \frac{2155}{0.91 + 1.91 + 2.35} = \frac{2155}{5.17} = 417$$

which is the same as q_{rc}. Now the temperature drops are recalculated:

$$
\begin{aligned}
t_1 - t_2 &= 417 \times 0.91 = 379 \\
t_2 - t_3 &= 417 \times 1.91 = 795 \\
t_3 - t_n &= 417 \times 2.35 = 981 \\
t_1 - t_n &= 2155
\end{aligned}
$$

The interface temperatures will then be 2021 and 1226°F.

The mean temperatures will be 2210, 1623, and 612°F. Taking new values for k and t_n of 242°F,

$$q = \frac{2400 - 242}{(9/9.9) + (4.5/2.39) + (2/0.81)} = \frac{2158}{0.91 + 1.88 + 2.47} = \frac{2158}{5.26} = 410$$

and $q_{rc} = 410$ as closely as can be read.

The values of temperature drops are

$$
\begin{aligned}
t_1 - t_2 &= 410 \times 0.91 = 373 \\
t_2 - t_3 &= 410 \times 1.88 = 772 \\
t_3 - t_n &= 410 \times 2.47 = 1013 \\
t_1 - t_n &= 2158
\end{aligned}
$$

Therefore the interface temperatures are 2027 and 1256°F, and the mean temperatures are 2213, 1641, and 627°F. By further trial, any degree of precision can be obtained, but the fourth trial here is sufficiently exact for ordinary purposes, as we do not know the conductivity values very accurately. Computing walls is a tedious process; but with experience, the initial selection of temperature will be fairly close to the final values. The heat flow and heat storage in a number of standard wall constructions are shown in Table 93.

7. Computation of Heat Flow in Cylinders. *Through Circular Structures.* Although the same general method is used for determining heat flow through circular structures, the equation for heat flow through a plane wall cannot be applied to flow through a cylinder if an accurate result is desired. The reason for this may readily be understood when it is considered that the inside circumference of a cylinder is smaller than the outside circumference. Consequently, heat spreads out as it travels from the inside to the outside, and conversely, it converges when the direction of flow is from the outside toward the inside.

Heat flow outward through a cylinder may be calculated by the following formulas:

1. For a wall of one material:

$$q = \frac{2\pi(t - t_n)}{(12/k_n) \ln (D_n/D)} \text{ Btu/(lin ft)(hr)}$$

or

$$q = \frac{t - t_n}{(12D_n/2k_n) \ln (D_n/D)} \text{ Btu/(sq ft)(hr)}$$

TABLE 93. HEAT LOSSES AND HEAT STORAGE CAPACITIES OF WALL STRUCTURES UNDER EQUILIBRIUM CONDITIONS*

(From *Bull.* R-2-H, Babcock and Wilcox Co.)

Thickness of wall, in.	Thickness of B & W insulating and fireclay brick (FB), in.	Hot-face temperature, °F															
		600		800		1000		1200		1400		1600		1800		2000	
		HL	HS	HL	HS	HL	HS	HL	HS	HL	HS	HL	HS	HL	HS	HL	HS
4½	4½K-16	67	398	100	564	138	742	180	928	226	1,130	278	1,320				
	4½K-20	89	538	128	760	175	1,000	230	1,250	290	1,505	350	1,775	420	2,040	468	2,320
	4½K-23	81	574	117	820	160	1,085	211	1,350	262	1,645	320	1,930	381	2,230	447	2,525
	4½K-26	137	867	202	1,230	273	1,620	350	2,010	434	2,430	528	2,850	626	3,280	736	3,720
	4½K-28	136	905	198	1,280	266	1,680	341	2,100	420	2,530	508	2,960	599	3,410	701	3,878
	4½K-30	176	1,170	261	1,660	356	2,170	460	2,700	574	3,270	697	3,830	835	4,420	985	5,000
	4½FB	547	3,970	809	5,610	1,095	7,260	1,400	9,000	1,727	10,720	2,082	12,450	2,442	14,240	2,820	16,080
7	7K-16	44	603	66	858	90	1,130	118	1,410	148	1,700	182	2,000				
	4½K-20 + 2½K-16	51	894	75	1,278	105	1,695	144	2,128	172	2,587	208	3,045	245	3,515	286	4,000
	4½K-23 + 2½K-16	47	945	67	1,355	94	1,790	126	2,235	163	2,710	195	3,195	235	3,669	280	4,165
	4½K-26 + 2½K-16	64	1,410	95	2,030	129	2,680	166	3,350	207	4,070	251	4,780	299	5,510	350	6,280
	4½K-28 + 2½K-16	65	1,470	96	2,120	130	2,800	169	3,510	212	4,260	260	5,040	313	5,860	372	6,690
	4½K-30 + 2½K-16	73	1,900	108	2,730	148	3,620	192	4,540	241	5,500	295	6,510	355	7,540	421	8,600
	4½K-30 + 2½K-23	80	1,920	125	2,750	167	3,620	209	4,580	267	5,580	322	6,629	385	7,650	437	8,750
	4½FB + 2½K-16	109	5,820	150	8,360	204	11,030	264	13,790	328	16,590	399	19,490	475	22,430	555	25,350
	4½FB + 2½K-23	114	6,062	170	8,500	230	11,100	293	13,890	366	16,625	442	19,550	522	22,485	608	25,500
	4½FB + 2½K-26	179	5,730	261	8,210	350	10,870	445	13,570	545	16,390	652	19,150	768	22,070	888	24,930
9	4½K-20 + 4½K-16	39	1,085	56	1,560	78	2,075	102	2,637	127	3,210	157	3,805	190	4,415	229	5,050
	4½K-23 + 4½K-16	37	1,140	54	1,625	73	2,155	99	2,735	122	3,320	150	3,935	178	4,565	210	5,210
	4½K-26 + 4½K-16	46	1,590	68	2,370	93	3,160	121	3,970	151	4,810	186	5,690	223	6,590	266	7,690
	4½K-28 + 4½K-16	46	1,730	67	2,470	92	3,250	119	4,080	148	4,930	180	5,810	215	6,730	253	7,650
	4½K-28 + 4½K-23	51	1,780	75	2,515	103	3,360	132	4,228	165	5,140	201	6,200	236	6,990	273	7,990
	4½K-30 + 4½K-16	50	2,160	74	3,120	102	4,130	132	5,190	166	6,270	203	7,400	244	8,570	290	9,790
	4½K-30 + 4½K-23	57	2,245	86	3,220	117	4,260	148	5,400	183	6,570	224	7,780	267	9,000	313	10,230
	4½FB + 4½K-16	61	6,100	91	8,810	126	11,610	163	14,540	204	17,530	248	20,580	294	23,680	344	26,860
	4½FB + 4½K-23	72	6,218	107	8,900	144	12,000	190	15,030	235	18,100	282	21,200	330	24,220	385	27,400
	4½FB + 4½K-26	118	6,280	172	9,010	231	11,930	294	14,920	362	18,000	433	21,170	510	24,350	592	27,560
9	9K-16	34	768	51	1,090	70	1,440	92	1,790	116	2,170	142	2,550				
	9K-20	46	1,050	67	1,505	86	1,995	117	2,470	147	2,955	177	3,450	210	3,985	248	4,510
	9K-23	41	1,085	58	1,550	80	2,080	108	2,640	135	3,170	164	3,365	192	4,280	225	4,880
	9K-26	72	1,650	106	2,340	142	3,060	182	3,810	225	4,600	273	5,400	324	6,230	380	7,080
	9K-28	71	1,710	104	2,440	140	3,160	178	3,970	220	4,800	264	5,630	312	6,480	362	7,360
	9K-30	94	2,190	138	3,110	188	4,090	242	5,070	302	6,140	366	7,230	436	8,330	513	9,450
	9FB	325	7,180	473	10,120	634	13,260	801	16,450	977	19,690	1,160	22,980	1,345	26,250	1,536	29,600

11½	11½K-16	27	977	40	1,390	55	1,830	72	2,280	91	2,740	111	3,230				
	9K-20 + 2½K-16	33	1,417	50	2,020	67	2,660	86	3,331	107	4,000	129	4,718	152	5,420	180	6,137
	9K-23 + 2½K-16	31	1,527	46	2,190	62	2,880	81	3,646	100	4,410	122	5,213	146	6,090	172	6,960
	9K-26 + 2½K-16	45	2,340	67	3,410	91	4,500	117	5,660	145	6,860	177	8,115	213	9,410	252	10,780
	9K-28 + 2½K-16	45	2,450	66	3,520	89	4,680	114	5,840	141	7,070	171	8,340	203	9,640	237	11,010
	9K-30 + 2½K-16	53	3,220	79	4,660	108	6,200	140	7,770	174	9,430	213	11,130	256	12,940	303	14,770
	9FB + 2½K-16	89	10,810	131	15,460	177	20,420	227	25,510	282	30,790	340	36,080	402	41,460	468	46,900
	9FB + 2½K-23	102	10,702	146	15,400	198	20,350	256	25,350	316	30,400	376	35,600	441	41,140	510	46,450
13½	9K-20 + 4½K-16	27	1,700	40	2,410	54	3,210	71	4,060	90	4,860	109	5,830	130	6,840	154	7,710
	9K-23 + 4½K-16	26	1,764	38	2,520	51	3,350	68	4,235	85	5,330	103	6,067	122	7,045	143	8,040
	9K-26 + 4½K-16	35	2,820	52	3,910	70	5,170	91	6,500	114	7,890	140	9,320	168	10,840	200	12,360
	9K-28 + 4½K-16	35	2,920	51	4,050	69	5,360	89	6,710	111	8,110	134	9,550	160	11,050	188	12,590
	9K-30 + 4½K-16	40	3,650	59	5,290	81	7,000	105	8,790	131	10,640	160	12,600	192	14,630	228	16,640
	9FB + 4½K-16	57	11,430	84	16,460	115	21,720	149	27,090	185	32,650	224	38,390	265	44,370	309	49,930
	9FB + 4½K-23	67	11,692	100	16,800	132	22,250	168	27,770	209	33,100	251	38,450	296	43,930	341	49,350
	9FB + 4½K-26	103	11,100	150	15,990	199	21,010	252	26,300	309	31,660	368	37,200	431	42,810	496	48,410
13½	9K-16 + 4½FB	33	1,040	49	1,570	68	2,080	89	2,650	112	3,260	137	3,760				
	9K-20 + 4½FB	43	1,466	64	2,050	88	2,725	113	3,422	140	4,200	168	5,070	198	6,020	231	7,010
	9K-23 + 4½FB	40	1,770	59	2,320	80	2,960	102	3,650	127	4,440	153	5,270	182	6,130	213	7,045
	9K-26 + 4½FB	67	2,350	98	3,410	132	4,480	169	5,610	209	6,790	253	8,000	300	9,240	353	10,570
	9K-28 + 4½FB	66	2,420	96	3,450	129	4,530	165	5,750	204	6,870	243	8,070	287	9,410	334	10,720
	9K-30 + 4½FB	85	3,160	125	4,500	169	5,930	218	7,420	271	9,030	330	10,750	393	12,360	462	14,270
	13½FB	233	10,230	338	14,520	448	18,950	563	23,510	684	28,180	809	33,000	934	37,800	1,067	42,700
16	13½FB + 2½K-16	80	15,390	118	22,160	159	29,200	202	36,410	250	43,850	300	51,420	352	58,990	407	66,770
18	9K-16 + 9FB	32	1,580	48	2,350	65	3,130	85	4,100	108	5,000	132	5,920				
	9K-20 + 9FB	42	2,283	63	3,215	84	4,270	106	5,325	131	6,500	158	7,800	190	8,860	227	10,050
	9K-23 + 9FB	38	2,527	50	3,420	73	4,403	99	5,505	124	6,470	149	7,800	177	9,000	205	10,250
	9K-26 + 9FB	62	3,390	90	4,850	122	6,410	156	8,100	193	9,900	235	11,760	280	13,710	329	15,780
	9K-28 + 9FB	61	3,470	89	4,940	120	6,540	153	8,210	188	9,960	226	11,750	266	13,720	310	15,690
	9K-30 + 9FB	77	4,480	114	6,420	154	8,550	198	10,700	246	13,120	300	15,600	356	18,180	419	20,940
	13½FB + 4½K-16	53	16,470	79	23,600	106	31,250	136	38,980	169	46,930	204	55,150	241	63,380	280	71,630
	13½FB + 4½K-23	62	16,432	91	23,200	123	31,000	156	39,222	192	47,200	230	55,500	271	64,150	315	72,700
20½	18FB	182	13,160	263	18,700	350	24,500	439	30,380	532	36,600	628	42,700	726	49,100	828	55,500
	18FB + 2½K-16	73	19,800	106	28,310	143	37,380	182	46,540	224	55,900	268	65,770	314	75,540	362	85,400
22½	18FB + 4½K-16	50	21,200	73	30,530	99	40,260	127	50,140	156	60,430	188	70,960	222	81,500	257	92,040
	18FB + 4½K-23	57	20,908	85	29,450	114	39,000	142	48,895	175	58,750	208	69,250	244	79,935	280	90,800
22½	22½FB	150	16,180	216	22,850	286	29,800	358	37,100	434	44,700	512	52,400	591	60,200	674	68,100

* HL = heat loss in Btu per sq ft per hr. Based on still air temperature of 80°F. HS = heat storage capacity in Btu per sq ft.

TABLE 93. HEAT LOSSES AND HEAT STORAGE CAPACITIES OF WALL STRUCTURES UNDER EQUILIBRIUM CONDITIONS* (*Continued*)

Thickness of wall, in.	Thickness of B & W insulating and fireclay brick (FB), in.	Hot-face temperature, °F															
		2200		2300		2400		2500		2600		2700		2800		2900	
		HL	HS	HL	HS	HL	HS	HL	HS	HL	HS	HL	HS	HL	HS	HL	HS
4½	4½K-16																
	4½K-20																
	4½K-23	510	2,830	545	2,985												
	4½K-26	855	4,170	921	4,400	987	4,630	1,062	4,870	1,135	5,180						
	4½K-28	806	4,350	864	4,570	921	4,770	980	5,050	1,042	5,290	1,105	5,540	1,173	5,780		
	4½K-30	1,146	5,610	1,235	5,920	1,325	6,220	1,424	6,530	1,520	6,840	1,628	7,170	1,735	7,470	1,857	7,790
	4½FB	3,210	17,770	3,410	18,750	3,580	19,600	3,780	20,500	3,960	21,400	4,160	22,280	4,350	23,150	4,550	24,100
7	7K-16																
	4½K-20 + 2½K-16																
	4½K-23 + 2½K-16	330	4,670	357	4,940												
	4½K-26 + 2½K-16	406	7,050	436	7,450	468	7,840	502	8,240	533	8,640						
	4½K-28 + 2½K-16	437	7,540	473	7,980	511	8,420	553	8,890	596	9,360	642	9,840	694	10,370		
	4½K-30 + 2½K-16	495	9,690	535	10,250	576	10,790	620	11,360	663	11,940	712	12,520				
	4½K-30 + 2½K-23	507	9,860	552	10,430	604	10,985	652	11,600	709	12,200	769	12,830	832	13,590	897	14,240
	4½FB + 2½K-16	639	28,260	682	29,790												
	4½FB + 2½K-23	701	28,550	747	29,100	797	31,670	845	32,200	895	34,700						
	4½FB + 2½K-26	1,020	27,870	1,084	29,280	1,155	30,740	1,223	32,220	1,295	33,700	1,372	35,200	1,448	36,560	1,525	38,050
9	4½K-20 + 4½K-16																
	4½K-23 + 4½K-16	249	5,865	274	6,195												
	4½K-26 + 4½K-16	313	8,510	339	8,990	366	9,500	396	10,020	427	10,550						
	4½K-28 + 4½K-16	294	8,600	316	9,050	339	9,550	364	10,050								
	4½K-28 + 4½K-23	316	8,960	340	9,450	368	9,960	395	10,480	422	10,960	450	11,480	478	11,930		
	4½K-30 + 4½K-16	340	11,010	367	11,640	396	12,280	429	12,930								
	4½K-30 + 4½K-23	362	11,560	388	12,200	418	13,000	450	13,490	482	14,200	518	14,880	558	15,580		
	4½FB + 4½K-16	399	29,940														
	4½FB + 4½K-23	440	30,450	467	32,200	496	33,820	523	35,750								
	4½FB + 4½K-26	678	30,780	721	32,400	766	33,970	812	35,600	860	37,170	907	38,750	958	40,380	1,010	42,020
9	9K-16																
	9K-20																
	9K-23	358	5,475	275	5,770												
	9K-26	442	7,930	474	8,370	510	8,820	546	9,260	586	9,710						
	9K-28	416	8,230	444	8,700	474	9,160	504	9,620	535	10,080	567	10,540	601	11,020		
	9K-30	596	10,580	640	11,180	686	11,750	734	12,400	785	12,980	840	13,600	889	14,180	946	14,800
	9FB	1,740	33,050	1,835	34,800	1,935	36,450	2,042	38,200	2,155	39,950	2,260	41,700	2,345	43,400	2,450	45,200

11½	11½K-16																
	9K-20 + 2½K-16																
	9K-23 + 2½K-16	200	7,850	214	8,310												
	9K-26 + 2½K-16	297	12,170	321	12,870	347	13,590	375	14,370	404	15,110						
	9K-28 + 2½K-16	275	12,380	294	13,070	314	13,790	335	14,490	358	15,220	385	15,980	408	16,700		
	9K-30 + 2½K-16	354	16,650	382	17,610	412	18,590	443	19,570	476	20,570	512	21,630	548	22,640	589	23,680
	9FB + 2½K-16	538	52,430	574	55,070	611	57,910	649	60,740	691	63,790						
	9FB + 2½K-23	577	52,100	616	55,000	658	57,710	676	60,800	712	64,900	746	66,800	784	70,000	822	73,100
13½	9K-20 + 4½K-16																
	9K-23 + 4½K-16	168	9,000	184	958												
	9K-26 + 4½K-16	235	13,980	255	14,830	275	15,670	297	16,490	219	17,360						
	9K-28 + 4½K-16	218	14,160	234	14,970	251	15,780	269	16,580	286	17,420	306	18,260	327	19,120		
	9K-30 + 4½K-16	268	18,790	290	19,890	312	21,000	337	22,140	363	23,260	390	24,400	420	25,610	451	26,810
	9FB + 4½K-16	357	55,900	382	58,890												
	9FB + 4½K-23	390	55,800	418	58,900	447	61,920	480	65,200	503	68,500	532	71,750				
	9FB + 4½K-26	564	54,120	600	56,970	634	59,810	670	62,560	708	65,420	746	68,360	784	71,110	825	73,850
13½	9K-16 + 4½FB																
	9K-20 + 4½FB																
	9K-23 + 4½FB	252	7,960	275	8,440												
	9K-26 + 4½FB	410	11,960	440	12,770	474	13,440	508	14,150	543	14,940						
	9K-28 + 4½FB	384	12,080	411	12,790	439	13,520	466	14,220	495	14,930	526	15,610	557	16,400		
	9K-30 + 4½FB	540	16,100	580	17,010	622	18,060	667	19,080	714	20,040	762	21,040	812	22,170	862	23,150
	13½FB	1,213	47,700	1,276	50,200	1,349	52,700	1,425	55,200	1,500	57,800	1,580	60,400	1,650	63,000	1,720	65,600
16	13½FB + 2½K-16	463	74,340	491	78,170	522	81,900	552	85,940	584	89,680	615	93,710	645	97,370	678	101,380
18	9K-16 + 9FB																
	9K-20 + 9FB																
	9K-23 + 9FB	236	11,450	255	12,130												
	9K-26 + 9FB	383	18,040	412	19,220	443	20,340	475	21,580	507	22,900						
	9K-28 + 9FB	356	17,650	380	18,820	406	19,900	432	21,010	459	22,160	487	23,300	515	24,430		
	9K-30 + 9FB	488	23,870	524	25,320	562	26,830	602	28,390	643	30,000	686	31,700	731	33,420	782	35,120
	13½FB + 4½K-16	320	79,870	342	83,950	364	88,220	385	92,300								
	13½FB + 4½K-23	360	81,600	382	86,300	406	90,783	441	95,550	460	100,300	485	110,200	513	120,100	541	130,100
20½	18FB	930	62,100	982	65,300	1,036	68,600	1,090	72,000	1,145	75,500	1,197	78,700	1,255	82,000	1,313	85,400
	18FB + 2½K-16	412	95,270	438	100,400	464	105,340	490	110,270	518	115,400	546	120,340	573	125,370	600	130,200
22½	18FB + 4½K-16	294	102,880	313	108,250	333	113,710	352	119,290	372	124,160						
	18FB + 4½K-23	317	102,250	341	108,200	362	114,165	384	120,300	407	126,500	431	132,700	456	139,000	482	145,350
22½	22½FB	757	76,200	802	80,200	844	84,200	886	88,400	930	92,400	971	96,500	1,015	100,700	1,060	105,000

* HL = heat loss in Btu per sq ft per hr. Based on still air temperature of 80°F. HS = heat storage capacity in Btu per sq ft.

2. For a composite wall:

$$q = \frac{2\pi(t - t_n)}{\frac{12}{k_1}\ln\frac{D_1}{D} + \frac{12}{k_2}\ln\frac{D_2}{D_1} + \cdots + \frac{12}{k_n}\ln\frac{D_n}{D_{(n-1)}}} \text{ Btu/(lin ft)(hr)}$$

or

$$q = \frac{t - t_n}{\frac{12D_n}{2k_1}\ln\frac{D_1}{D} + \frac{12D_n}{2k_2}\ln\frac{D_2}{D_1} + \cdots + \frac{12D_n}{2k_n}\ln\frac{D_n}{D_{(n-1)}}} \text{ Btu/(sq ft)(hr)}$$

where q = the quantity of heat, Btu hr
t_1 = the hot-face temperature
t_n = the cold-face or casing temperature
D = the inside diameter of cylinder, in.
D_1 = the outside diameter of inside lining material, in.
D_2 = the outside diameter of secondary lining material, in.
$D_{(n-1)}$ = the outside diameter of next to last lining material, in.
D_n = the outside diameter of outside lining material, in.
k_1 = the thermal conductivity of inside lining material
k_2 = the thermal conductivity of secondary lining material
k_n = the thermal conductivity of outside lining material

k_1, k_2, and k_n are expressed in Btu/(hr)(sq ft)(in.)(°F)

Interface temperatures between various layers are expressed as
t_1 = the temperature at D_1, °F
t_2 = the temperature at D_2, °F
$T_{(n-1)}$ = the temperature at $D_{(n-1)}$, °F

For a case in which the flow of heat is from the outside of the cylinder toward the center, D would become the outside or largest diameter and D_n the inside or smallest diameter.

8. Flow of Heat through Furnace Walls under Variable Conditions. The temperature distribution in a simple or composite wall can be computed approximately for conditions of unsteady heat flow mathematically or graphically by the method of Schmidt. Such calculations require values of diffusivity for each material over the whole temperature range and, at best, are only approximate. For a discussion of this method, which requires too much space to treat here, reference should be made to Trinks[16] or Schack.[45] Composite walls require a very complicated set of calculations.

Practically, the problem can be solved quite readily by constructing a small section of the wall as the side or door of a furnace. Couples on the faces and between the layers will give the temperature distribution accurately. The value of q passing out from the wall can be estimated fairly closely from the outside temperature. Recently electrical analogues of heat-flow systems have been made up for solving unsteady-state problems.

The case of dynamic heat flow in cylinders has been treated by Gurney and Lurie,[8] and convenient monographic charts have been made up by Davis.[79]

CHAPTER XIX

SIZES AND TOLERANCES

1. Standard Shapes. A standard shape is a refractory brick other than a straight $9 \times 4\frac{1}{2} \times 2\frac{1}{2}$-in. size that is generally stocked by all refractory manufacturers in the United States and England. The German[16] standard brick is $250 \times 123 \times 65$ cm. Although all manufacturers do not agree as to what constitutes a standard shape, there are many universally accepted ones that may safely be specified in any design work.

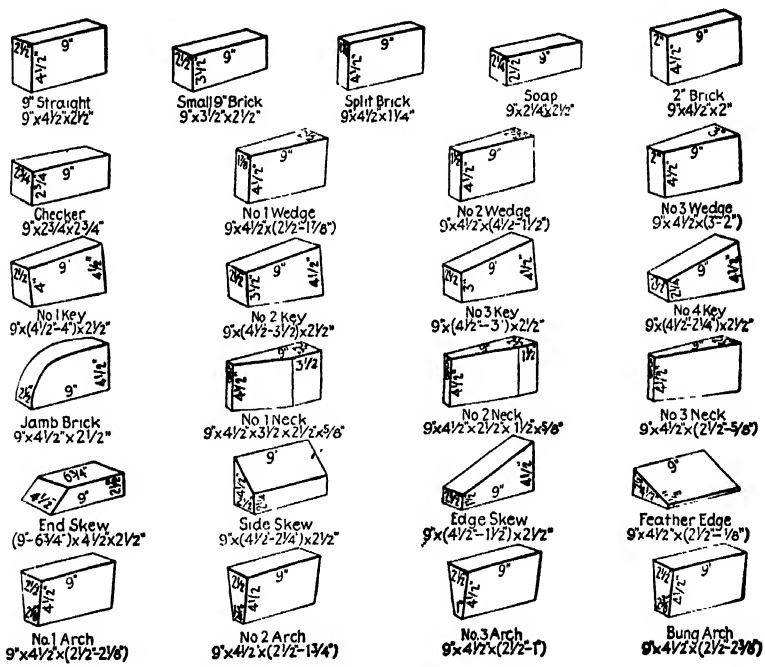


FIG. 307. Standard shapes (9-in. series).

Standard shapes are used in all types of construction to save cutting straight brick, as illustrated in Chap. XXVII.

In Figs. 307 and 308 are given the sizes of the generally accepted standard firebrick shapes. Of course, many others are stocked as standard by individual companies, and these will be treated separately as special shapes.

The size tolerance on standard shapes and straight brick is given by the American Society for Testing Materials as ± 2 per cent, which covers both

shrinkage and warpage on all dimensions over 4 in. On dimensions less than this, a tolerance of 3 per cent is specified. ASTM Method C 134–41 is used in measuring. Warpage is measured by laying a straightedge along a concave diagonal and inserting a calibrated wedge under the straightedge at the center of the tile. The American Refractories Institute recommends that warpage should not exceed 1 per cent of the diagonal,[13] according to Method C 154–41.

Silica standard shapes are approximately the same as firebrick shapes. Magnesite and chrome refractories can be called standard only in the sim-

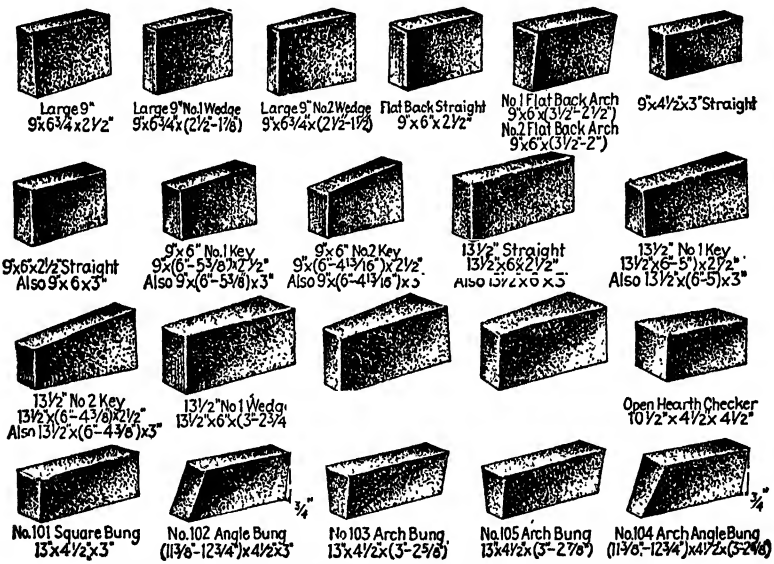


FIG. 308. Standard shapes of firebrick (larger than 9 in.).

pler shapes of the 9-in. series. The manufacturer's catalogue should always be consulted, as shapes stocked by one company might not be stocked by another.

2. Special Shapes. *Glass-tank Blocks.* Shapes that are used only for certain particular types of construction can be obtained from stock at times but are not generally available without ordering ahead. This class includes glass-tank blocks. Unfortunately there is little standardization of these blocks, but a few of the favorite sizes are listed in Table 94.

Glass-tank blocks, or flux blocks as they are usually termed, are generally made with more care than other large shapes. The clays are carefully blended and aged; the molding is carried out in such a way as to give a homogeneous structure; and the faces of the block are often ground accu-

rately to dimensions. Besides the rectangular blocks, there are many special blocks used in tanks, such as the throat blocks.

TABLE 94

Common Sizes of Flux Blocks for Continuous Tanks

12 × 18 × 24 in.	12 × 18 × 42 in.	12 × 24 × 36 in.
12 × 18 × 30 in.	12 × 18 × 48 in.	12 × 24 × 42 in.
12 × 18 × 36 in.	12 × 24 × 30 in.	12 × 24 × 48 in.

Common Sizes of Flux Blocks for Day Tanks

8 × 12 × 24 in.	8 × 18 × 24 in.	8 × 24 × 30 in.
8 × 12 × 30 in.	8 × 18 × 30 in.	8 × 24 × 36 in.
8 × 12 × 36 in.	8 × 18 × 36 in.	8 × 24 × 42 in.
	8 × 18 × 42 in.	

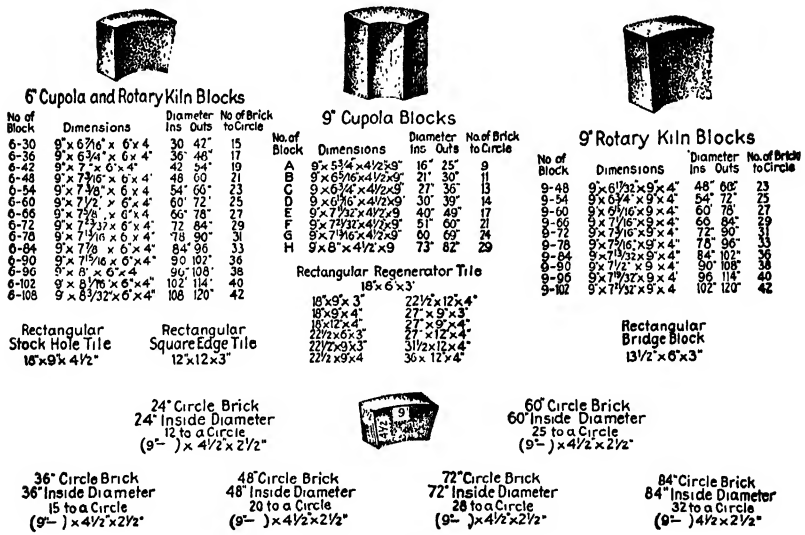


FIG. 309. Shapes and sizes of radial blocks.

Cupola and Rotary-kiln Blocks. These blocks are segments of a ring and are used to form a cylindrical lining. The common sizes are given in Fig. 309. Many manufacturers carry these blocks as standard shapes.

Cupola blocks are generally made of a dense fireclay, but rotary-kiln blocks are usually made of a high-alumina clay or magnesite, as these materials seem to resist the slag action well and hold a good coating of clinker.

Tile. Rectangular tile of fireclay may usually be obtained in the sizes shown in Table 95.

Checker Brick. These generally are available in the following size:

$$10\tfrac{1}{2} \times 4\tfrac{1}{2} \times 4\tfrac{1}{2} \text{ in.}$$

TABLE 95. COMMON SIZES OF FIRECLAY TILE

2 × 9 × 12 in.	3 × 6 × 18 in.	4 × 9 × 18 in.
2 × 12 × 12 in.	3 × 6 × 22½ in.	4 × 9 × 22½ in.
2 × 12 × 15 in.	3 × 9 × 18 in.	4 × 9 × 27 in.
2 × 12 × 18 in.	3 × 12 × 12 in.	4 × 12 × 18 in.
2 × 12 × 24 in.		4 × 12 × 22½ in.
		4 × 12 × 27 in.
		4 × 12 × 36 in.
6 × 12 × 36 in.	8 × 18 × 42 in.	
6 × 12 × 42 in.	8 × 18 × 48 in.	
6 × 12 × 48 in.	8 × 18 × 54 in.	
6 × 18 × 36 in.	8 × 24 × 42 in.	
6 × 18 × 42 in.	8 × 24 × 48 in.	
6 × 18 × 48 in.	8 × 24 × 54 in.	
6 × 24 × 42 in.		
6 × 24 × 48 in.		

Malleable Furnace Shapes. Certain shapes are made especially for malleable-iron furnaces. They include

Bung arch,	9 × 4½ × (2½ to 2⅜) in.
	13½ × 4½ × (3 to 2⅝) in.
	13½ × 4½ × (3 to 2⅞) in.
Square bung,	13½ × 4½ × 3 in.
Angle bung,	(13½ to 12⅛) × 4½ × 3 in.
Tap-out block,	9 × 7½ × 7½ in.

Lime-kiln Brick. Some special lime-kiln brick are made by a few manufacturers, usually of silica or high-alumina material.

Hot-blast Stove Checker Brick. A number of stove-brick shapes are made for particular types of structure. They are stocked by several manufacturers.

Coke-oven Shapes. Shapes for making up rectangular and beehive ovens are more or less standardized by a number of manufacturers. Shapes for by-product ovens are also stocked, but the number of shapes is so large that they cannot well be listed here.

Blocks for Suspended Arches. There are a number of patented constructions for suspended arches requiring rather complicated blocks. One type of arch block is shown in Fig. 310. More details are given in Chap. XXVII.

Boiler Shapes. There are a number of shapes used in stationary and locomotive boilers that are stocked by some manufacturers.

Other Special Shapes. In addition to these, many special shapes are made for a particular installation, such as burner tile, impeller disks, hollow blocks, and feed-hole bricks. A special shape is shown in Fig. 311.

The Design of Special Shapes. When designing a new furnace, it is often necessary to have special shapes made up. It should be remembered that

special shapes, particularly when in small quantities, are relatively expensive and should be used only where they are necessary. A special shape should be made as simple as possible because complications increase the mold cost and do not permit as careful molding. Undercutting or thin projections should be avoided. It is also undesirable to specify thin slabs or bars because the loss by warping is apt to be large. In general, the shape should be as compact as possible and not exceed 24 in. in length. However, shapes can be made 48 in. long if necessary. A small shape generally has a better structure than a large one and is burned more evenly. Therefore

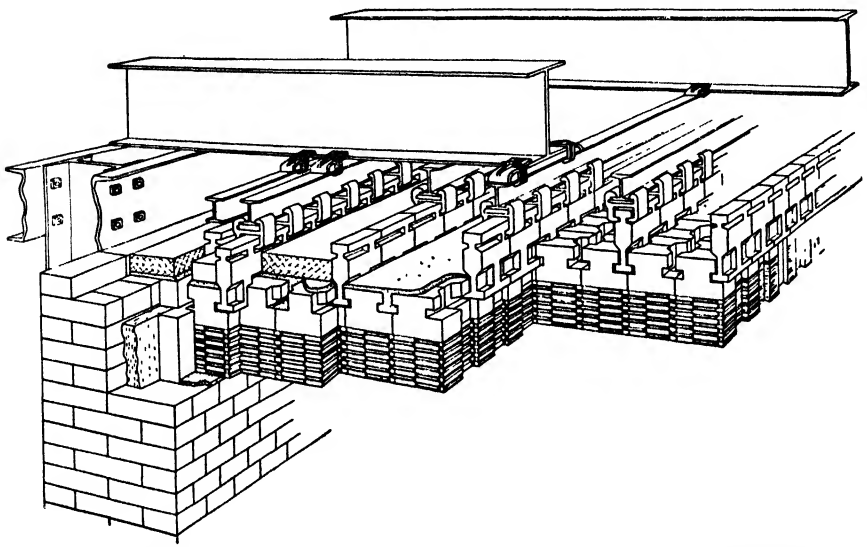


FIG. 310. Special shapes used in a detrick suspended-arch construction. (*Courtesy of the M. H. Detrick Company.*)

the size of shapes should always be kept as small as practical. In designing special shapes to be used in conjunction with straight brick, a good rule to follow is to make the vertical dimensions a multiple of $2\frac{9}{16}$ in. and the horizontal a multiple of $4\frac{9}{16}$ in. (the thickness and width of a straight brick plus one joint).

3. Kiln Furniture. A considerable volume of refractories is used as kiln furniture, *i.e.*, supports and containers for ceramic ware while it is being fired. As the furniture must be heated and cooled with the ware, it is desirable to keep its mass down to a minimum in order to permit a more rapid heating and cooling cycle and increase the kiln efficiency. Because of the frequent temperature changes, the furniture must be able to resist spalling fairly well; and in many cases, it must be able to support a heavy load at high temperatures.

Saggers. Saggers are refractory boxes for holding whiteware. They serve partly as a support and partly as muffles to protect the ware from the kiln gases. The saggers are generally piled one on top of the other in bungs as shown in Fig. 312. A wadding of soft clay is placed between the saggers to make a tight joint. The ware is supported in the saggers in a variety of ways, which we need not consider here.

FIG. 311. Burner tiles. (*Courtesy of Babcock & Wilcox Company.*)

Saggers are made in a number of shapes and sizes, a few of which are shown in Fig. 313. However, there is no generally accepted standard. The wall thickness varies between $\frac{3}{8}$ and $\frac{7}{8}$ in. with an average of about $\frac{5}{8}$ in. The composition varies but generally consists of a grog (usually crushed saggers with the fines removed), a plastic clay to give strength, and a fireclay to prevent too much vitrification. A good body should have a low coefficient of thermal expansion and an elastic structure, as explained in Chap. XV. Talc is often used as an ingredient in modern sagger bodies.

The average life of a sagger was often no more than 25 cycles ten or fifteen years ago due to a poor body, nonhomogeneous molding, rough han-

dling, and, perhaps most important, lack of thorough preburning. As the sagger expense in the whiteware industry is a large item, a really superior sagger is well worth while. Many manufacturers have experimented to some extent on saggers, and the National Bureau of Standards has carried on a considerable investigation of this subject. Now the sagger life is often 50 to 100 cycles.

Another trouble with saggers is the separation of particles from the interior of the sagger, which may fall on the glazed ware and form serious

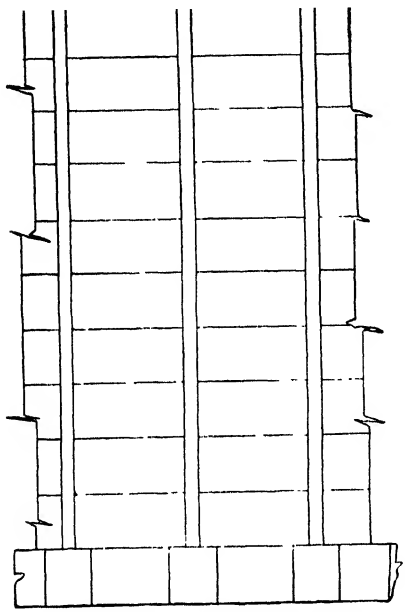


FIG. 312. Saggers piled in bungs.

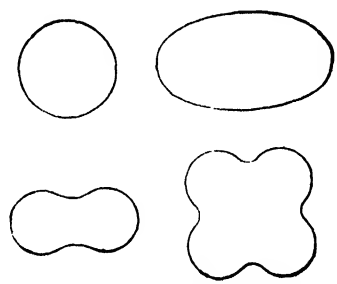


FIG. 313. Common shapes of saggers.

defects. A sagger therefore must have a firm, smooth surface, and it is the usual practice to paint over the inside of the sagger with a wash of some low-vitrifying compound to form a sort of glaze.

Saggers are made in a number of ways. Formerly they were all made by hand on a wooden form. This method requires considerable labor, but it was traditionally believed that first-class saggers could be made only by this method. Later they were made on a machine press, of which there are many kinds. Recently a large proportion of saggers have been made by casting a slip into a plaster mold.

Other materials have been used for saggers, such as silicon carbide, mullite, and zircon, but as yet they have not shown enough superiority over fireclay at moderate temperatures to warrant their increased cost.

Slabs and Posts. In many cases, ware does not have to be protected from the kiln gases, so that supports as shown in Fig. 314 can be used. Generally the slabs are made of fireclay, fused alumina, silicon carbide, or zircon from ⅝ to 2½ in. thick, depending on the size and load. Important advances have been made in open-setting kiln furniture in the last few years. Open settings permit 25 to 100 per cent more ware[17] to be fired in a given volume and so have replaced the sagger largely in the whiteware industry for bisque firing.

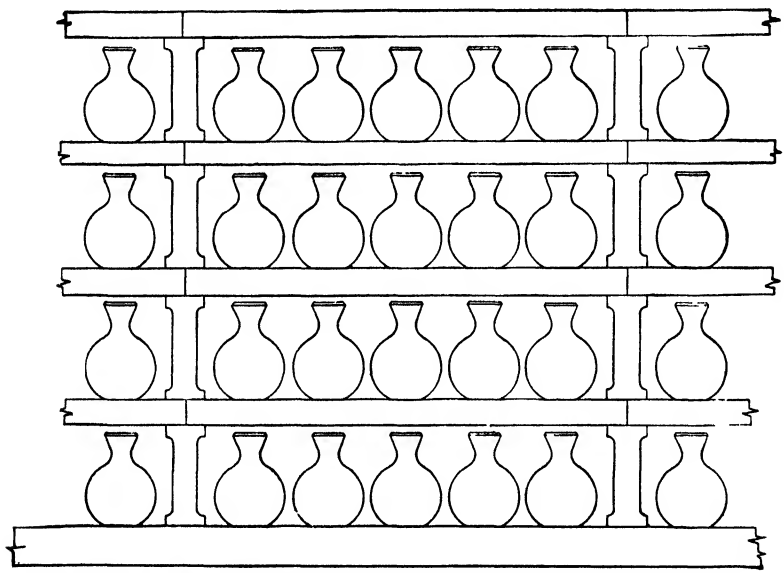


FIG. 314. Setting tile where ware needs no protection from the atmosphere.

TABLE 96. REFRACTORY SLABS FOR OPEN-KILN SETTING

	Inches
Sanitary ware for straight T.K.	24 × 36 × 1¼
	24 × 36 × 2¼
	32 × 25 × 1¼
	17 × 25 × 1¼
	18 × 24 × ¾
General ware and electrical porcelain for straight T.K.	25½ × 21½ × 1
	20½ × 22½ × ⅞
Circular T.K.	32 × 16½ × 18½ × 1
	32 × 16½ × 18½ × ¾
	28 × 16½ × 18½ × ¾
	28 × 16½ × 18½ × ½
	32 × 16½ × 18½ × ¾
	32 × 16½ × 18½ × ½

4. Muffles. Muffles are generally used for enameled ware and for other articles when it is desired to keep them free from the furnace gases. Large muffles are constructed of sections of thin tile as shown in Fig. 315. The thickness is kept as low as possible, from ¾ to 1¼ in., in order to obtain the maximum rate of heat transfer. Sometimes each tile has its center recessed to an even thinner wall. The materials used for the muffle are fireclay, fused alumina, and silicon carbide. The high conductivity of the last two materials is of great advantage in this construction.

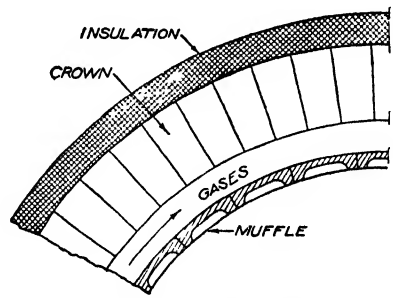


Fig. 315. A large muffle.

Small muffles are used in many laboratory types of furnace. Fireclay, fused-alumina, and silicon-carbide types can be obtained in many sizes. Small muffles of fused silica are available but cannot be used at high temperatures. A few of the common sizes of fireclay muffles are listed in Table 97.

Table 97. Common Sizes of Fireclay Muffles

Length, in.	Width, in.	Height, in.
7	3	2¼
8	4¾	3
10½	5¼	3⅞
12	6	4
12	8	5
15	9	5¾
16	10	5½
18	12¼	7¾
19	10½	6½

5. Retorts. Fireclay retorts for gas manufacture are from 7 to 10 ft long and about 18 in. wide. The wall thickness is 2½ to 3 in. in order to withstand the load. Since carbon closes up the pores when it is in use, the structure need not be dense but should be able to resist spalling.

The body is usually made of about equal parts of plastic clay and grog. As in the case of saggers, the fine particles of the grog are removed. The retorts are usually hand-molded onto a form, but pressed retorts have been used. The finished retorts are burned in a vertical position in a firebrick kiln, and sometimes they are glazed. The more modern continuous retorts are vertical with a height of 40 to 50 ft. They are made up from silica

shapes as shown in Fig. 316. A strong, dense structure is desired to prevent the lining from coming off as a result of carbon deposited in the pores.

6. Crucibles. Crucibles are made of a great variety of refractory materials and in many shapes and sizes. It is, of course, impossible to list all of them here, but a few common sizes will be described.

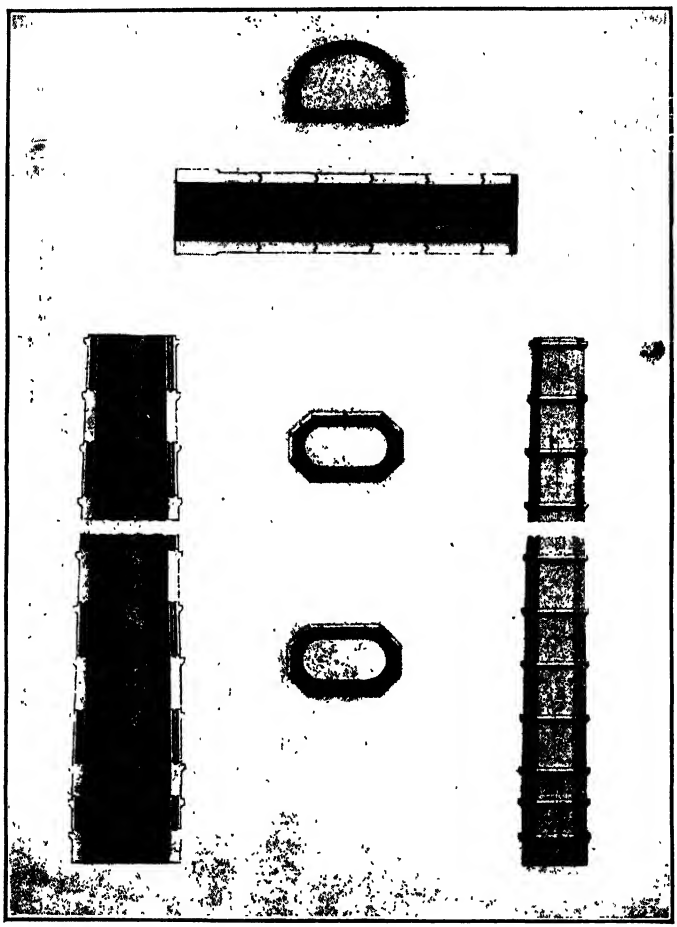


FIG. 316. Silica retorts for gas production. (*Courtesy of Harbison-Walker Refractories Company.*)

Clay Crucibles. Clay crucibles are made from fireclay and grog. The small ones are pressed, and the large ones made on a jigger or flower-pot machine. The clay crucibles are generally used in small sizes for assaying, roasting, and low-temperature melting. Common shapes are shown in Fig. 317.

The usual sizes of this clay crucible (Denver Fire Clay Company) are shown in Table 98.

TABLE 98. COMMON SIZES OF CLAY CRUCIBLES

Size	Height, in.	Diameter at top, in.
G	5⅝	3⅝
H	5⅞	3¾
I	6	4
J	6⅝	4⅜
K	7¼	4¾
L	8	5¼
M	8¼	5¾
N	9⅜	6½
O	10	7
P	11	7¾
Q	12	8¼
R	13	9⅜

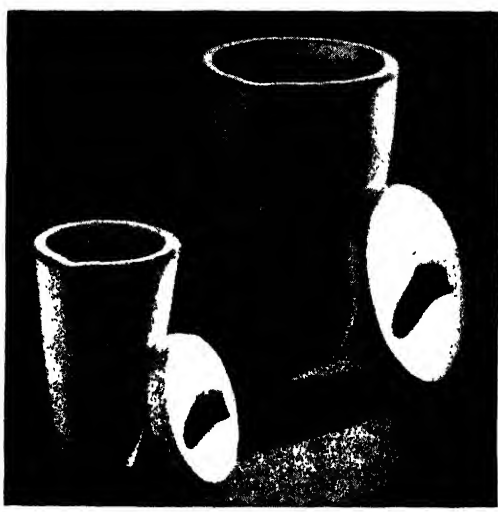


FIG. 317. Clay crucibles. (*Courtesy of the Joseph Dixon Company.*)

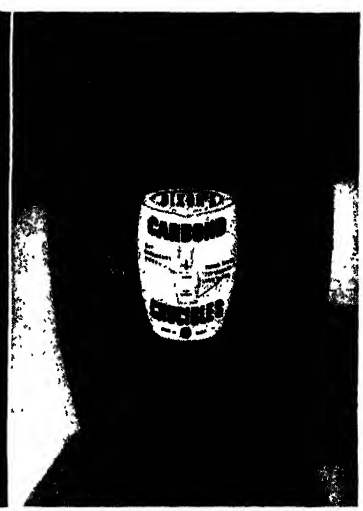


FIG. 318. A clay-graphite crucible. (*Courtesy of the Joseph Dixon Company.*)

Graphite Crucibles. Graphite crucibles are extensively used for metal melting. The graphite increases the thermal conductivity and gives a strong body at high temperatures. These crucibles are made of a mixture of plastic fireclay and flake graphite. The amount of graphite varies between 6 and 50 per cent. The clay and graphite are thoroughly mixed

in a wet pan or pug mill and aged. The crucibles are formed on a jigger in the same manner as fireclay crucibles. The shape found most suitable for this type of crucible is shown in Fig. 318. A large number of standard sizes are available as given in Table 99 (Dixon).

TABLE 99. COMMON SIZES OF GRAPHITE CRUCIBLES

Number (Dixon)	Outside diameter, in.	Outside height, in.
0	1½	2
00	1⅞	2⅜
000	1⅞	2½
0000	2⅜	3
1	3⅛	3⅝
2	3¾	4½
3	4¼	5¼
4	4⅝	5⅝
5	4⅞	6
6	5¼	6¼
7	5½	6¾
8	5¾	7¼
10	6	8
14	6¾	8½
18	7⅜	9¾
20	7¾	10¼
	up to	up to
400	19 1⅛6	24 5⅛6

In Chap. XII some special crucibles are described, but no size standards have been evolved.

7. Glass Pots. Glass pots are made of a suitable mixture of clays and grog. Before the First World War, most of the American manufacturers imported their glass-pot clays. Since then, domestic clays have been used successfully in nearly all cases. As a result of the work of the National Bureau of Standards,[1,15] the old hand-molded pots have been largely superseded by cast pots.

Apparently there are no generally accepted standards of size for pots, but covered pots are often 45 × 58 × 52 or 46 × 60 × 52 in. in width, length, and height, respectively. A typical covered pot is shown in Fig. 319.

8. Refractory Porcelain. Refractory porcelain is used mainly for laboratory ware, spark plugs, and pyrometer protection tubes. It must have a high softening point, a dense structure, and a resistance to spalling as high as possible.

The high-mullite porcelains, sometimes made from calcined sillimanite

or kyanite, are much used. However, they require high firing, preferably up to 1650°C (about 3000°F). Lately sintered alumina fired at 1800°C (about 3270°F) has been used for severe conditions.

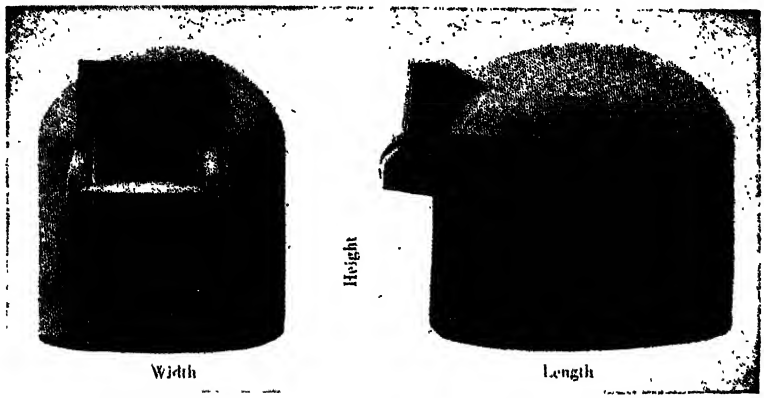


FIG. 319. Covered glass melting pot. (*Courtesy of Findlay Clay Products Company.*)

TABLE 100. COMMON SIZES OF REFRACTORY PORCELAIN TUBING

Type	Outside diameter, in.	Hole diameter, in.	Length, in.
Insulating tubing, 2-hole	1/8	1/32	1–18
	1/4	5/64	1–48
	3/8	7/64	1–60
Insulating tubing, 1-hole	3/32	1/16	1–12
	5/32	1/16	1–18
	1/4	1/8	1–48
Insulating tubing, 4-hole	3/16	3/64	1–36
	5/16	1/16	1–48
Protection tubes, closed end	1/4	1/8	6–18
	3/4	9/16	6–48

The forming and firing of high-temperature porcelains are discussed in Chap. XII.

It is necessary to glaze some high-temperature porcelains to prevent passage of gases. Perhaps the most complete study of high-temperature glazes is that by Sortwell.[3]

Refractory porcelain can be obtained in a large variety of sizes, glazed or unglazed. In Table 100 are shown some common sizes.

CHAPTER XX

MISCELLANEOUS PROPERTIES OF REFRACTORIES

1. Measurement of Particle Size. *Screen Analysis.* The determination of the particle-size distribution in a granular material is of considerable importance in ceramic work. For materials coarser than 150 to 300 mesh,

TABLE 101. UNITED STATES STANDARD SIEVE SERIES

Meshes per lineal inch	Sieve number	Sieve opening, inches	Sieve opening, millimeters	Wire diameter, inches	Wire diameter, millimeters
2.58	2½	0.315	8.00	0.073	1.85
3.03	3	0.265	6.73	0.065	1.65
3.57	3½	0.223	5.66	0.057	1.45
4.22	4	0.187	4.76	0.050	1.27
4.98	5	0.157	4.00	0.044	1.12
5.81	6	0.132	3.36	0.040	1.02
6.80	7	0.111	2.83	0.036	0.92
7.89	8	0.0937	2.38	0.0331	0.84
9.21	10	0.0787	2.00	0.0299	0.76
10.72	12	0.0661	1.68	0.0272	0.69
12.58	14	0.0555	1.41	0.0240	0.61
14.66	16	0.0469	1.19	0.0213	0.54
17.15	18	0.0394	1.00	0.0189	0.48
20 16	20	0.0331	0.84	0.0165	0.42
23.47	25	0.0280	0.71	0.0146	0.37
27 62	30	0.0232	0.59	0.0130	0.33
32.15	35	0.0197	0.50	0.0114	0.29
38.02	40	0.0165	0.42	0.0098	0.25
44.44	45	0.0138	0.35	0.0087	0.22
52.36	50	0.0117	0.297	0.0074	0.188
61.93	60	0.0098	0.250	0.0064	0.162
72.46	70	0.0083	0.210	0.0055	0.140
85.47	80	0.0070	0.177	0.0047	0.119
101.01	100	0.0059	0.149	0.0040	0.102
120.48	120	0.0049	0.125	0.0034	0.086
142.86	140	0.0041	0.105	0.0029	0.074
166 67	170	0.0035	0.088	0.0025	0.063
200.00	200	0.0029	0.074	0.0021	0.053
238 10	230	0.0024	0.062	0.0018	0.046
270.26	270	0.0021	0.053	0.0016	0.041
323.00	325	0.0017	0.044	0.0014	0.036

screens are used to separate the material into any desired number of grades; but for the finer materials, air- or water-separation methods are most satisfactory.

The United States standard series of sieves is based upon a 1-mm opening, the larger and smaller screens varying as $\sqrt{2}$, or 1.414. The characteristics of this series of screens are given in Table 101.

The Tyler screens are more commonly used. They have as a basis a 200-mesh screen with an opening of 0.0029 in., and the sizes of openings also

TABLE 102. TYLER SCREEN SERIES

Openings, inches	Openings, millimeters	Mesh per lineal inch	Diameter of wire, inches
1.050	26.67		0.148
0.883	22.43		0.135
0.742	18.85		0.135
0.624	15.85		0.120
0.525	13.33		0.105
0.441	11.20		0.105
0.371	9.423		0.092
0.312	7.925	2½	0.088
0.263	6.680	3	0.070
0.221	5.613	3½	0.065
0.185	4.699	4	0.065
0.156	3.962	5	0.044
0.131	3.327	6	0.036
0.110	2.794	7	0.0328
0.093	2.362	8	0.0320
0.078	1.981	9	0.0330
0.065	1.651	10	0.0350
0.055	1.397	12	0.0280
0.046	1.168	14	0.0250
0.0390	0.991	16	0.0235
0.0328	0.833	20	0.0172
0.0276	0.701	24	0.0141
0.0232	0.589	28	0.0125
0.0195	0.495	32	0.0118
0.0164	0.417	35	0.0122
0.0138	0.351	42	0.0100
0.0116	0.295	48	0.0092
0.0097	0.246	60	0.0070
0.0082	0.208	65	0.0072
0.0069	0.175	80	0.0056
0.0058	0.147	100	0.0042
0.0049	0.124	115	0.0038
0.0041	0.104	150	0.0026
0.0035	0.088	170	0.0024
0.0029	0.074	200	0.0021

vary as the $\sqrt{2}$. The intermediate sizes are available to give closer spacing. In Table 102 are given the characteristics of this series.

A sample to be screened should be completely dry, and the lumps broken up. It can then be passed through any required number of screens in series. Care must be taken, however, to shake the screens long enough to pass all undersized material through. A convenient piece of apparatus for making screen analyses is shown in Fig. 320. In some cases, wet screening is used, for example, to separate clay from grog.

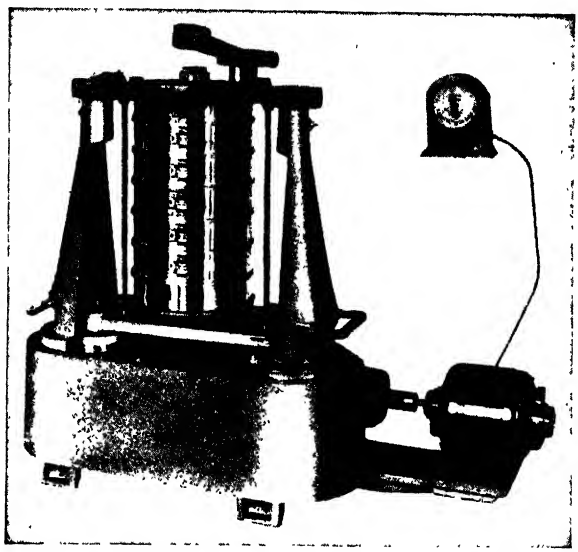


FIG. 320. A shaking apparatus for making screen analyses. (*Courtesy of the W. S. Tyler Company.*)

TABLE 103. EXAMPLE OF SCREEN DATA

Screen	Weight, grams	Per cent	Cumulative per cent
On 4	0.5	0.5	0.5
On 6	1.5	1.5	2.0
On 8	3.0	3.0	5.0
On 10	6.5	6.5	11.5
On 14	10.0	10.0	21.5
On 20	15.5	15.5	37.0
On 28	20.0	20.0	57.0
On 35	21.5	21.5	78.5
On 48	14.0	14.0	92.5
On 65	5.5	5.5	98.0
On 100	1.0	1.0	99.0
Through 100	1.5	1.5	100.5

A convenient method to make an analysis is to weigh out a sample of, say, 100 g. In obtaining this sample, the greatest care is necessary to ensure that it is representative. The sample is then passed through the desired screens, and the amount remaining on each screen is weighed. This weight in grams will give the percentage directly. A typical analysis is shown in Table 103.

There are a number of methods of plotting the results of a screen analysis. The fraction of each particular size of particle may be plotted on a frequency curve, as in Fig. 321, or the cumulative percentage may be plotted

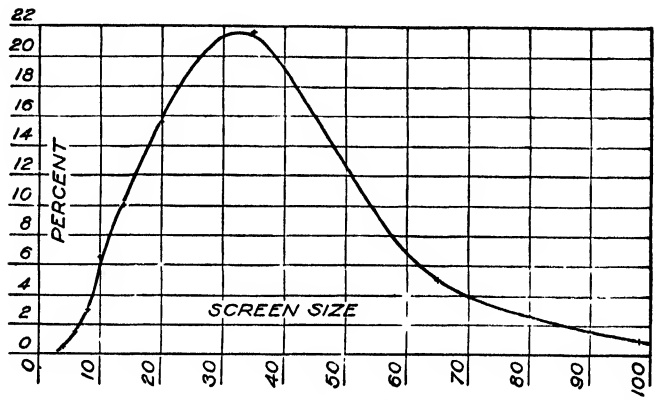


FIG. 321. The result of a screen analysis. The fraction of each particle size plotted as a frequency curve.

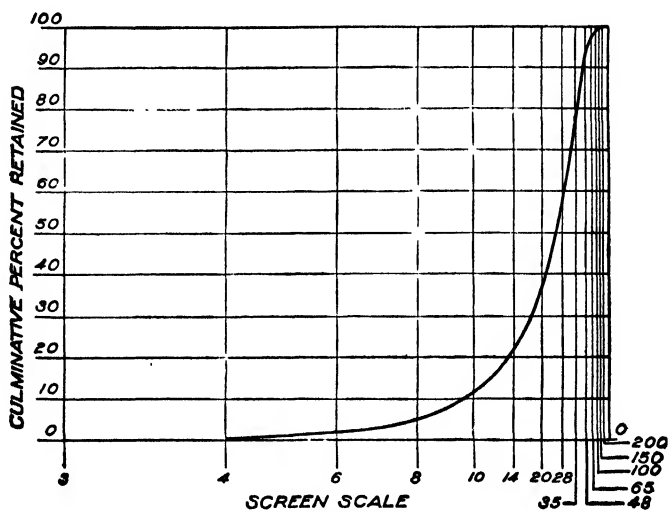


FIG. 322. Result of a screen analysis.

on logarithmic paper as is often done when using the Tyler screens (Fig. 322). Many attempts have been made to express the size distribution by means of a single factor. The work of Hatch and Choate[17] gives, perhaps, the best representation. They found that if logarithms of the sizes were plotted against the percentages of each size, a very close approach to a probability curve resulted in all cases. This curve can be expressed by two parameters, M_g and σ_g. M_g and σ_g can be determined graphically by plotting experimental data on log-probability paper. The references at the end of the chapter will give many other viewpoints of this problem. The extensive work on fine grinding by Martin[9] and others deserves careful study.

Settling Methods. In order to determine the particle-size distribution in a finely divided material such as a clay, the settling rate of the particles in water is found to be their most useful property. Using Stokes' law, which states that a sphere of diameter D will fall at a velocity V in a liquid of viscosity η when the density of the particle is S_1 and of the liquid S_2, the diameter is found by

$$D = \sqrt{\frac{18\eta V}{(S_1 - S_2)g}}$$

in cgs units.

It might be thought that the irregular or platelike particles would settle at a different rate from equivalent spheres; but with the exception of extreme plates such as are found in mica, Stokes' law is found to hold down to 1 μ diameter and probably lower. The work of Wadell[21] and Norton and Speil[23] confirms this.

One of the most important factors in this measurement is the complete dispersion of the particles in water. If they are flocculated to any extent, the results will be greatly in error. In the case of clays, considerable agitation is needed to break up clumps in addition to a deflocculating agent such as silicate of soda, sodium pyrophosphate, sodium carbonate, or Daxad. The state of dispersion should be checked with the microscope before the settling test.

When the particles are below 1 μ in diameter, the settling rate becomes so slow that it must be accelerated by centrifugal force. As most of the particles in a clay are within this region, a special centrifuge (Fig. 323) has been developed recently for measurements down to 0.05 μ. The amount of suspended material at any one time is determined by the specific gravity of the suspension as measured by a special hydrometer bulb. The pipette method[24] of drawing off a small volume of suspension and drying down to find the suspended matter is slightly more precise than the hydrometer but more time-consuming.

The standard test method used in the Ceramic Laboratory at the Massachusetts Institute of Technology is given below as taken from the *Journal of the American Ceramic Society*[23] and is based on the work of Casagrande.[19]

A 13-g sample of the clay is shaken in 300 cc of distilled water to which has been added 0.13 g (1 per cent) of Daxad No. 23 (Dewey & Almy Chemical Co.). This is put through a hand homogenizer (Central Scientific Co., No. 70180) and transferred to a quart fruit jar. The jar is attached to a ball-mill frame and tumbled end over end at 60 rpm for 5 days.

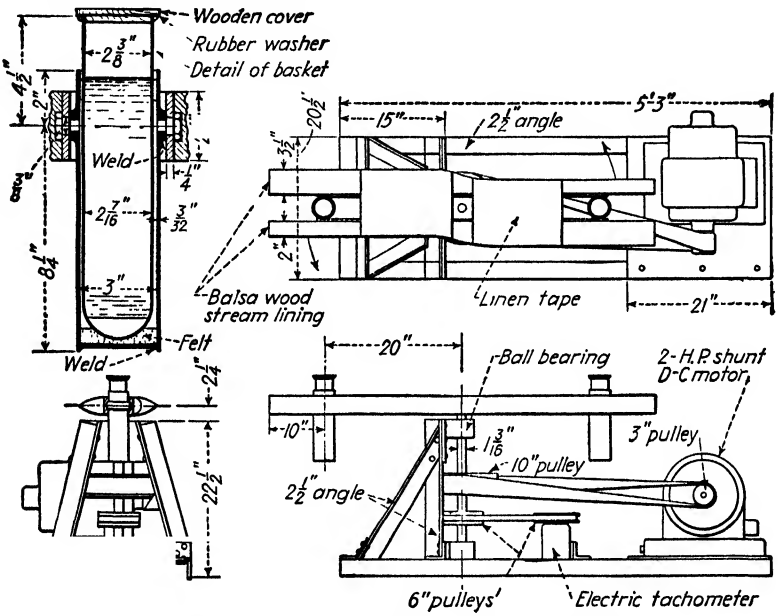


FIG. 323. Long-arm centrifuge. (*J. Am. Ceram. Soc.*)

The sample is then transferred to the glass container, used in the centrifuge, and diluted to exactly 650 cc. A 1,000-cc graduate is filled with a solution of 0.2-g Daxad No. 23 in 1,000 cc of distilled water to be used as a standard in checking the hydrometer. Just before starting a run, the sample is shaken end over end to form a homogeneous suspension; sheet rubber is tied over the top to prevent spilling. The time is taken from the instant the container is placed in the metal basket of the centrifuge. After ½ min, the hydrometer bulb is carefully inserted into the suspension, and the specific gravity is read at the top of the meniscus exactly 1 min from the start of the test. The bulb is first immersed slightly deeper than the equilibrium position to assure a good meniscus. About 20 sec is allowed for the insertion or removal of the hydrometer to prevent eddy currents. The stem of the bulb must always be kept clean to obtain a good meniscus.

Two different samples are run concurrently in the present centrifuge; the second is started 12 min after the first sample to prevent any necessity of hurrying the early readings. After the first 10 min of the test, every specific gravity reading in the suspension is accompanied by a corresponding reading taken in the standard solution also at the top of the meniscus. The temperatures of these two are adjusted to be equal within 0.3°C at the start of the test, and they

TABLE 104

Time interval	Speed, r.p.m.	Total equivalent time of gravity settling
Minutes:		Minutes:
1	Stationary	1
2	Stationary	3
2	Stationary	5
5	Stationary	10
10	Stationary	20
10	Stationary	30
30	Stationary	60
Hours:		Hours:
1	Stationary	2
1.5	Stationary	3.5
2.5	Stationary	6
Minutes:		
30	125	10.3
15	200	15.8
30	200	27
30	300	52
30	400	95
30	500	164
30	550	247
Hours:		
1.25	600	493
1.75	600	835
3	600	1,420
3.5	600	2,110
4.5	600	2,980
8	600	4,550

are kept equal throughout the run. In this way, temperature corrections for the hydrometer are eliminated, because the value sought is the difference in specific gravity between the two and not the actual value of the specific gravity of the suspension. Temperature readings, precise to within ±0.2°C, are taken in each container for every test point, and the temperature is kept as constant as possible during a run. The hydrometer, when not in actual use, is wiped off and placed in the graduate containing the clear Daxad solution. The times at which the

specific gravity should be read were determined arbitrarily to divide the region between 50 and 0.1 μ into 20 approximately equal divisions when the data are plotted on semilogarithmic paper. Table 104 gives these time intervals, speed of rotation, and the total elapsed time of equivalent gravity settling, based on an effective centrifuge radius of 49 cm.

In using the centrifuge, the elapsed time was taken between starting the centrifuge and shutting off the current to the motor. The acceleration and deceleration were rapid enough so that this approximate procedure was justified. The starting and stopping, however, must not be so sudden as to cause swirling of the suspension. In the tests carried out, the first day's run extended through 493 hr so that any short interval of gravity settling after that time was practically negligible.

To change the data obtained from the sedimentation run into a distribution curve, the particle size or equivalent spherical diameter corresponding to each reading must be determined, as well as the percentage of material finer than this size. Using Stokes' law, the size which has settled to the center of the hydrometer bulb is easily obtained from the Casagrande nomographic chart.* It is necessary to calibrate only the distance-settled scale of the chart against the specific-gravity scale of the particular hydrometer used. Directions for this and also a key to the chart are given on the chart itself.

In using this distance-settled scale, a small meniscus correction (about 0.0003) must be added to the hydrometer reading, inasmuch as the actual distance settled is from the surface of the suspension (not the top of the meniscus) to the center of volume of the bulb. The value used on the temperature scale of the chart, which corrects for the temperature effect on the viscosity of water, should be the average over the test period up to the time of that reading.

For effective settling periods of more than 50 hr, better accuracy can be obtained with the chart by taking advantage of the fact that the size is given by the equation

$$D = kt^{-1/2}$$

where D = the diameter
t = the time

Thus the equivalent time is divided by a factor of 100; and using this new time value, the size obtained from the chart is divided by 10 to give the correct value. The reason for this step is to avoid large slopes between corresponding points on adjacent scales, a condition which decreases the accuracy of values obtained from the chart.

To determine the percentage of material finer than any given size, the following equation is used:

$$W \text{ per cent} = \frac{S}{S-1} \times \frac{100}{C} (R - d) \times 10^8$$

* These charts can be obtained from Julius Springer in Berlin, or from the Soil Mechanics Laboratory, Massachusetts Institute of Technology, Cambridge, Mass.

where S = the specific gravity of suspended material
C = the concentration of suspended matter, g/liter
$R - d$ = the difference in specific gravity between suspension and corresponding standard reading at same temperature

The specific gravity of the clay can be obtained in a pycnometer bottle but runs close to 2.58 for kaolinite types of clays. To make this method clearer, an actual example is worked out in Table 105.

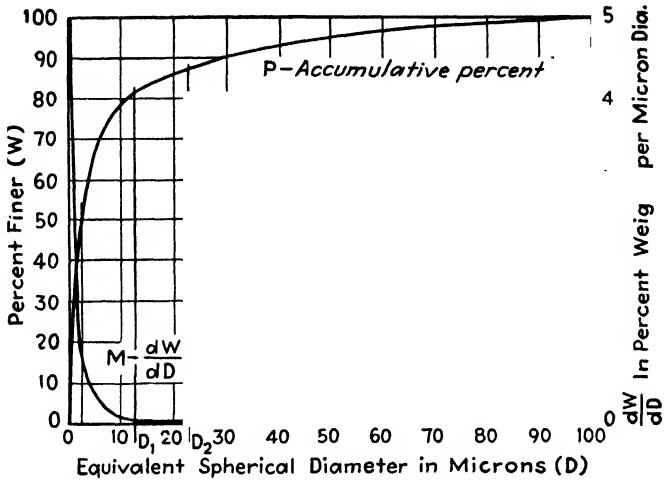


FIG. 324. Size distribution for a typical clay plotted with linear coordinates. (*J. Am. Ceram. Soc.*)

The graphical representation of the results of a size analysis is generally carried out by plotting the weight per cent, W, finer than a given size as ordinates against that size, D, as abscissas. This method is shown in curve P of Fig. 324. A better picture of the distribution, however, can be obtained by plotting the function dW/dD against D as in curve M. This curve represents the slope of P and the area under it between any sizes D_1 and D_2 will be

$$\int y\,dx = \int_{D_2}^{D_1} \frac{dW}{dD}\,dD = \int_{W_{D_2}}^{W_{D_1}} dW = W_{D1} - W_{D2}$$

Therefore the weight of particles between D_1 and D_2 in Fig. 324 is equal to

$$\text{Total weight of sample} \times \frac{\text{area between } D_1 \text{ and } D_2}{\text{total area under } M}$$

For example, the line at 50 per cent W cuts the P curve at 2.3 μ, through which a vertical line divides the area under M into two equal parts.

The distribution curve in Fig. 324 brings out strikingly the fact that clays have a large proportion of the particles in a very narrow range of sizes. The curve, however, is so crowded into the fine end that little precision is possible in reading the plot in this range. For this reason, it has been found better to plot

TABLE 105

Time	Centrifuge speed, r.p.m.	Acceleration × gravity	Equivalent settling time	Temperature, °C.	Reading R	Blank d	$R + C$	Size, microns	$(R - d) \times 10^3$	Per cent
			Minutes							
9.12	0	1.0								
9.13	0	1.0	1	24.2	1.0106	0.9996	1.0109	29.0	11.0	91.7
9.15	0	1.0	3		1.0103		1.0106	17.2	10.7	88.8
9.17	0	1.0	5		1.0097	0.9996	1.0100	13.8	10.1	84.2
9.22	0	1.0	10		1.0092		1.0095	10.0	9.6	80.0
9.32	0	1.0	20	24.2	1.0084	0.9995	1.0087	7.4	8.8	73.0
9.42	0	1.0	30		1.0078	0.9995	1.0081	6.15	8.2	68.5
			Hours							
10.12	0	1.0	1	24.5	1.0070	0.9995	1.0073	4.5	7.5	62.5
11.12	0	1.0	2	24.4	1.0060	0.9995	1.0063	3.3	6.5	54.4
12.42	0	1.0	3.5	23.9	1.0054	0.9997	1.0057	2.5	5.7	47.5
3.42	0	1.0	6.5	23.7	1.0048	0.9998	1.0051	1.92	5.0	41.9
3.49–4.16	125	8.6	10 3	24.2	1.0043	0.9997	1.0046	1.54	4.6	38.6
4.29–4.44	200	22.0	15.8	24.5	1.0039	0.9995	1.0042	1.25	4.4	36.6
5.00–5.30	200	22.0	26.8	24.1	1.0030	0.9996	1.0033	1.00	3.3	27.8
5.40–6.10	300	49.5	51.5	23.8	1.0023	0.9997	1.0026	0.73	2.6	21.6
6.19–6.49	400	88.0	95.5	24.9	1.0015	0.9993	1.0018	0.56	1.9	15.8
6.58–7.28	500	137.0	164	25.7	1.0003	0.9991	1.0006	0.42	1.2	10.4
7.39–8.09	550	166.0	247	25.7	1.0000	0.9991	1.0003	0.35	0.9	7.6
11.16–12.31	600	196.0	492	26.3	0.9994	0.9990	0.9997	0.25	0.4	3.6
1.00–2.45	600	196.0	834	27.1	0.9990	0.9988	0.9993	0.19	0.2	1.7
3.00–6.00	600	196.0	1422	28.0	0 9986	0.9985	0.9989	0.145	0.1	0.8
9.00–12.30	600	196 0	2107	28.1	0 9986	0.9986	0.9989	0.12	0.0	0.0
1 00-5 00	600	196 0	2990	27.7	0 9988	0 9988	0.9991	0.10	0.0	0.0

the same data on semilog paper as in Fig. 325. Here the characteristics of the distribution in the fine fractions are brought out clearly, but the areas under the distribution curve have to be corrected for the scale if they are used quantitatively. As in Fig. 324, the line passing through 50 per cent of W cuts the P curve at 2.3 μ and divides the plotted area under M into two equal parts. The actual area on the diagram, however, is quite different on the two sides of the line. The experimental points on the P curve show the consistency of the observations.

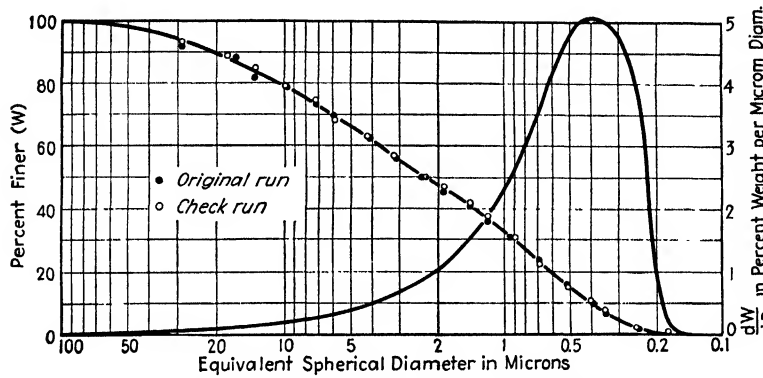


FIG. 325. Size distribution for a typical clay plotted on semilogarithmic paper. (*J. Am. Ceram. Soc.*)

The diver method of measuring particle size as developed by Berg[25] is most ingenious and consists of adding to the suspension tiny glass floats of known density which will always maintain a level consistent with the density of the suspension at that point. Therefore by plotting the settling rate of these floats, the density changes in the suspension can be followed with no disturbance.

Gaudin and Hukki[29] suggest plotting the logarithm of the cumulative per cent finer against the logarithm of the size. This has the great advantage of producing a straight line in most cases.

Other Methods. Elutriation[22] with either water or air as a medium can be used for the measurement of particle size, but this method is more useful for producing definite-size fractions.

The microscope allows direct measurement of the particle sizes with a calibrated eyepiece.[27] The lower limit, however, is about 1 μ, but certain problems can well be handled by this method.

For finer sizes, the electron microscope gives us the only direct means of particle size measurement down to less than 0.1 μ.

The X-ray diffraction pattern allows the calculation of particle sizes from 0.05 μ and less by the line broadening that occurs with small particles. This method may also be used to measure the size of crystals in a lump of refractory.

A number of other methods have been used but are of minor importance in ceramics.

Interpretation of Particle Size. The mean diameter of a single particle is clear when considering a sphere or cube where the diameter or edge respectively are definite measures. In the case of a parallelepiped with sides a, b, and c, we can express four mean diameters as follows:

$$dm = \frac{a + b + c}{2} \qquad \text{(Statistical)}$$

$$dm = \sqrt{\frac{2ab + 2ac + 2bc}{6}} \qquad \text{(Side of a cube of equal area)}$$

$$dm = \sqrt[3]{abc} \qquad \text{(Side of a cube of equal volume)}$$

$$dm = \frac{3abc}{ab + ac + bc} \qquad \text{(Harmonic mean relating surface to volume)}$$

For platelike particles the various dm's vary a great deal, so the type of mean diameter should always be specified. The spherical mean diameter is usually taken as the diameter of a sphere settling at the same rate as the given particle.

When considering an evenly graded series of particles, the following mean diameters for the series may be written

$$d_{ms} = \frac{\Sigma nd}{\Sigma n} = \frac{1}{2}\frac{d_1^2 - d_2^2}{d_1 - d_2} = \frac{1}{2}(d_1 + d_2) \qquad \text{(Statistical mean)}$$

$$d_{me} = \frac{\Sigma nd^2}{\Sigma nd} = \frac{2}{3}\frac{d_1^3 - d_2^3}{d_1^2 - d_2^2} \qquad \text{(Length mean)}$$

$$d_{ma} = \frac{\Sigma nd^3}{\Sigma nd^2} = \frac{3}{4}\frac{d_1^4 - d_2^4}{d_1^3 - d_2^3} \qquad \text{(Area mean)}$$

$$d_{mv} = \frac{\Sigma nd^4}{\Sigma nd^3} = \frac{4}{5}\frac{d_1^5 - d_2^5}{d_1^4 - d_2^4} \qquad \text{(Volume mean)}$$

where n = the total number of particles
d_1 = the smallest diameter in the series
d_2 = the largest diameter in the series

The so-called "Mellor mean" is often used

$$dm = \sqrt[3]{\frac{(d_1 + d_2)(d_1^2 + d_2^2)}{4}}$$

but does not seem to be based on any experimental evidence.

To illustrate the use of the various mean diameters, the following example based on an actual microscopic count by Perrott[7] on an evenly graded series of particles is given in Table 106.

TABLE 106

Fraction diameter, microns	60	50	40	30	20	10	6	2
No. of particles	87	100	156	660	1,750	6,200	25,600	155,000
Percentage of total based on:								
Number $\frac{n}{\Sigma n}$	0.05	0.05	0 1	0.3	0.9	3.3	13.5	81.8
Length $\frac{nd}{\Sigma nd}$	0.9	0 9	1.1	3.5	6.1	10.9	22.4	54.3
Area $\frac{nd^2}{\Sigma nd^2}$	7.8	6.3	6.3	14.9	17.6	15.5	16.1	15.6
Volume $\frac{nd^3}{\Sigma nd^3}$	22.5	14.9	11.9	21.3	16.7	7.4	3.8	1.5

Calculating the mean diameter for the whole series gives

$$d_{ms} = \sum \left(\frac{n}{\Sigma n} \cdot d \right) = \frac{\Sigma nd}{\Sigma n} = 3.0\ \mu$$

$$d_{mc} = \sum \left(\frac{nd}{\Sigma nd} \cdot d \right) = \frac{\Sigma nd^2}{\Sigma nd} = 7.0\ \mu$$

$$d_{ma} = \sum \left(\frac{nd^2}{\Sigma nd^2} \cdot d \right) = \frac{\Sigma nd^3}{\Sigma nd^2} = 21.0\ \mu$$

$$d_{mv} = \sum \left(\frac{nd^3}{\Sigma nd^3} \cdot d \right) = \frac{\Sigma nd^4}{\Sigma nd^3} = 36.4\ \mu$$

The physical significance of these values can be visualized by assuming that all the particles in the sample were laid out in a line, each particle touching the next and each being smaller than the one preceding it. If the particle in this line was selected that had equal numbers of particles above and below it, its diameter would be 3.0 μ. On the other hand, if a particle were selected exactly in the center of the line, it would have a diameter of 7.0 μ. A particle selected so that the total area or volume of all the particles above or below it were equal would have a diameter respectively of 21.0 and 36.4 μ. This brings out the fact that a mean particle size has no significance unless the type of mean is specified.

2. Structure. The macrostructure of refractories is of importance because a homogeneous material is seldom encountered. The size and shape of the pores, the shape of the grog particles, and the extent of the bonding are of interest. By a study of the structure, the manufacturing methods may be improved to produce a better product.

A cross section of a brick can be ground to a flat surface on a cast-iron wheel with coarse carborundum and water. The brick is then dried and

heated enough to flow red sealing wax over the surface and into the pores. This surface can now be polished with a fine abrasive. The contrast between the light refractory and the dark sealing wax should bring out the structure very clearly. The structure of a kaolin brick prepared in this way is shown in Fig. 326.

FIG. 326. Structure of a kaolin refractory. The surface of this refractory was ground to a rough surface and then the pores were filled with sealing wax. The surface was then given a finer polish.

3. Permeability. *Importance in Refractories.* The flow of gases through refractory walls is important in many furnaces, especially where large pressure differences exist, as in recirculating types. Also the permeability of such parts as thermocouple tubes, muffles, and recuperators is of interest in efficient design.

Permeability is also of value as a check on the manufacture, as laminations, voids, and soft spots are shown up in the permeability test. In the case of heat insulators, this property is useful in indicating the extent of interconnecting pores.

Measurement of Permeability. Absolute permeability is the property of the refractory and does not in any way depend on the fluid. It may be expressed as

$$\lambda = \eta \frac{Q}{A} \cdot \frac{l}{(P_1 - P_2)} \cdot \frac{1}{t}$$

where λ = the absolute permeability
η = the viscosity of the fluid, poises
Q = the volume of gas flowing at mean pressure $(P_1 + P_2)/2$, cc
A = the area, sq cm
l = the length of path, cm
P_1 = the exit pressure, dynes/sq cm
P_2 = the entrance pressure, dynes/sq cm
t = the time, sec

The dimensions of this equation are L^2 = area. However, our usual meas-

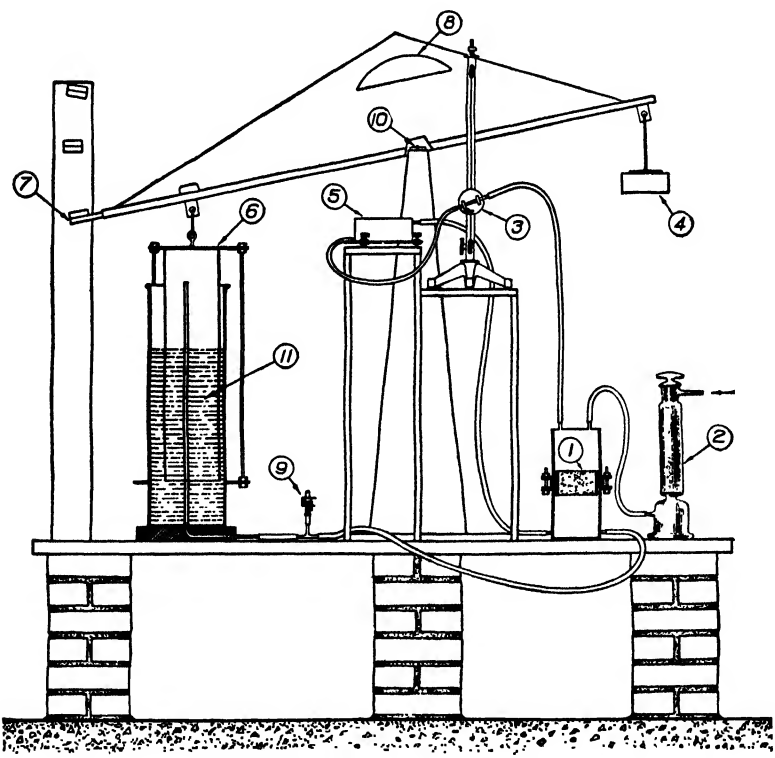


FIG. 327. Permeability apparatus.

urements of permeability are with a particular fluid such as air at room temperature, so that the measured permeability k is expressed by

$$\frac{\text{Volume of gas} \times \text{length of path}}{\text{Area} \times \text{time} \times \text{pressure difference}}$$

which has the dimension

$$\frac{L^2}{ML^{-1}T^{-1}} = \frac{\text{area}}{\text{viscosity}}$$

k is usually expressed as cc/(cm)(sq cm)(sec)(cm of water) or as cu ft/(in.)(sq ft)(min)(in. of water pressure).

Permeability can be measured on small cylindrical or cubical specimens, but a more representative value is obtained on a whole brick with air passing through as it does in the wall. Permeability tests of whole wall sections give data in regard to the joints and bricks together, but little work has been reported along these lines.

A precise and convenient apparatus for the measurement of permeability is shown in Fig. 327 as developed in the Ceramic Laboratory of the Massachusetts Institute of Technology. The specimen 1 is cemented tightly into the holder with beeswax. Air is drawn through the drying

TABLE 107

Run No.	1	2	3	4	5	6
Weight on end of beam, g.	200	200	400	400	1,000	1,000
Mercury below atmospheric pressure, mm.	0 85	0 85	1.70	1 70	4 21	4 24
Atmospheric pressure, mm. mercury	757 40	757 40	757 40	757.40	757 40	757 40
Pressure in gasometer, mm. mercury	756 55	756.55	755 70	755 70	753 16	753.16
Temperature, °C.	29.0	29.1	28.4	28.3	28.0	28.1
V (from chart), volume of air at standard conditions passed through specimen, cc.	.604	1,604	1,595	.595	1,592	1,592
P_0, zero reading of manometer	1.16	1.16	1.06	1.05	1.06	1.06
P_1, final reading of manometer	1 41	1.40	1.52	1.51	1 94	1 94
$P_1 - P_0$, pressure difference, cm. alcohol	0 25	0 24	0.46	0 46	0.88	0.88
Specific gravity of alcohol	0.801	0.801	0.801	0.801	0 801	0.801
P, pressure difference, cm water	0.20	0.19	0.37	0.37	0.71	0.71
t, time, sec.	119	120	68	69	34	34
K, permeability	5.6	5 7	5.3	5.3	5.5	5.5

Area of specimen = 78.5 sq. cm. Thickness = 6.5 cm.

power 2 and the specimen by the suction of the gasometer 6 filled with oil 11 and counterweight 4 using a beam pivoted at 10. The latter is calibrated so that as it moves through a definite distance by the pointer 7, which can be timed with a stop watch to pull a known volume of air through the specimen. The balance weight 8 compensates for the buoyancy of the gasometer cylinder. The difference in pressure between the two sides of the

TABLE 108. PERMEABILITY OF FIREBRICKS (BURNED)

Type of clays	Manufacturing method	Permeability, cc per sec per cm cube per cm head of water
Flint, semiflint, and plastic	Semidry press	0 0066
New Jersey plastic	Hand molded	0 0092
Semiflint	Soft mud	0 011
Flint and semiflint and plastic	Soft mud	0 012
Second grade semiflint and plastic	Soft mud	0 016
Plastic	Soft mud	0.017
Semiflint	Soft mud	0.033
Cheltenham plastic	Dry press	0.049
Flint and semiflint	Hand molded	0.069
Flint and plastic	Hand molded	0 11
Flint and plastic	Soft mud	0.13
Grog, flint, and plastic	Soft mud	0.14
Pennsylvania clay	Dry press	0.15
Second grade semiflint and plastic	Dry press	0.19
Sillimanite and clay	Hand molded	0.45
Silicon carbide, recrystallized	Dry press	0.80
Clay and carbon, insulating	Dry press	1.20
Insulating firebrick, 3.5 lb		2.6
Insulating firebrick, 3 lb		3.1
Insulating firebrick, 2 lb		5.5

specimen is measured by the alcohol manometer 3 with its reservoir 5. The method of testing will be made clear by Table 107 for a typical run.

Permeability values for several refractories are shown in Table 108, and additional values are given in the references.[40,41,42,48]

4. Strength of Refractories. The cold strength of fired refractories is not generally of importance in itself; however, it often serves as a guide to other characteristics such as vitrification, burning temperature, or purity of material. In the case of heat insulators, the strength is of value in determining the ability to withstand handling and shipping. The ASTM Standard method for cold crushing strength is given in C 133–39, a method that should be followed to obtain consistent results. For insulating brick,

C 93–46 should be used. In Table 109 are given values of crushing strength. The strength of many pure materials is given in the tables of Chap. XII.

TABLE 109. CRUSHING STRENGTH OF REFRACTORIES

Material	Crushing Strength, lb per sq in.
Fireclay brick	2,000–12,000
Bauxite brick	6,000
Silica brick	3,000–5,000
Zirconia	7,000
Magnesite	5,000–8,000
Chrome	6,000
Insulating brick	50–500

5. True Density. The following method has been found satisfactory for the determination of true density: The material is powdered through at least 100 mesh, dried at 105°C until thoroughly dry, and placed over $CaCl_2$ until at room temperature. About 1 g is weighed into the previously calibrated and weighed pycnometer bottle. The bottle is filled about one-half full of freshly boiled distilled water and is kept at 60°C for about ½ hr, and the contents agitated to wet the particles thoroughly and remove entrapped air. The bottle is next placed under a vacuum to make certain that all air has escaped. The reduced pressure should not be strong enough to boil the water violently, since loss is likely to occur. About 20 min of treatment using an ordinary aspirator pump is sufficient.

The bottle is then filled to the mark with distilled water and placed in a constant-temperature bath for 1 hr, whereupon the bottle is carefully capped; the capillary and the outside of the bottle wiped clean; and the whole weighed.

The specific gravity is calculated from

$$\text{Specific gravity} = \frac{W - P}{(W_1 - P) - (W_2 - W)}$$

where P = the weight of pycnometer and stopper
W = the weight of pycnometer and stopper and sample
W_1 = the weight of pycnometer and stopper full of water
W_2 = the weight of pycnometer and stopper and sample and water

Tetrahychonaphthalene or tetrachlorethane, because of their low viscosity and high wetting properties, are useful in the case of nonplastics in place of water, as the boiling and deairing steps are eliminated. Values on the same sample should check to ± 0.005.

6. Abrasion Resistance. Refractories used in the hearths of furnaces or other places where objects are slid along them must have a good resistance to abrasion. Furthermore, refractories are often worn away by particles in a rapidly moving gas. Abrasion tests at room temperature, such as

are regularly used for paving brick and tiles, mean little for refractories because the conditions are far different at high temperatures. In the first place, the refractory must have a strong, well-bonded structure, and second, it must not become plastic at the working temperature. In general, it has been found that a brick which shows good resistance to load will also resist abrasion.

Abrasion has been measured at room temperature by the Bauschinger disk grinder, the sand blast of Bradshaw and Emery,[1] and the rattler test of the National Paving Brick Manufacturers' Association. None of these tests, however, is used at the working temperature of the refractory. Perhaps the most logical tests are those proposed by Hancock and King.[2] Here samples of the refractory are rubbed together inside a furnace, and the loss in weight determined for a certain time of test. To show the effect of temperature, a specimen was tested as follows:

Temperature of Test	Loss in Weight, g
20°C (68°F)	0.115
1050°C (1922°F)	0.255

This shows that the abrasion resistance decreases with the temperature. It was also concluded that a fine-grained structure and a high-burning temperature increase the abrasion resistance.

The abrasion resistance of an insulating firebrick is naturally less than for a heavy refractory, although hard coatings are helpful. Abrasion tests have been made on this material by circulating fine particles by means of a high-velocity air stream through a duct lined with a particular brick.

7. Electrical Resistivity. In electric-furnace work, the electrical resistance of refractories is of considerable importance, and there are many other cases where a high-temperature electrical insulator is desirable.

The method of measuring the resistivity is theoretically simple but at high temperatures is beset by numerous practical troubles; however, at temperatures up to 1000°C (1832°F), the apparatus is comparatively simple. The methods used by the National Bureau of Standards,[54] King,[57] Northrup,[60] and Brace[62] are substantially the same. A comparatively high voltage is placed across the specimen, and the current flow measured with a sensitive ammeter or similar device. The greatest difficulty is to reduce the contact resistance, and a number of methods have been used to prevent this error. Henry[55] and a few others used alternating current of 1,000 cycles to prevent electrolytic effects.

In Table 110 are given some values of electrical resistivity obtained by different experimenters.

It will be noticed that the values given in the following table are rather discordant in some instances. This may be due in part to the variation in specimens and in part to errors in experimentation.

TABLE 110. ELECTRICAL RESISTIVITY, OHMS PER CENTIMETER CUBED

Material	Firing temperature	Temperature of test				
		700°C (1297°F)	1000°C (1832°F)	1200°C (2192°F)	1400°C (2557°F)	1500°C (2732°F)
Chemical porcelain[1]	1400°C (2550°F)	84,000	20,000			
Bureau Standards porcelain #152[1]	1450°C (2640°F)	550,000	251,000			
Beryl[1]	1355°C (2470°F)	51,000				
Spinel[1]	1485°C (2700°F)	Infinite	High			
Sillimanite[1]	1485°C (2700°F)	Infinite	120,000			
Kyanite[1]	1485°C (2700°F)	Infinite	95,000			
Andalusite[1]	1485°C (2700°F)	570,000	130,000			
Periclase[1]	1485°C (2700°F)	Infinite	Infinite			
Ohio flint clay[2]	1500°C (2732°F)	15,800	2,120	1,050	721	582
Kaolin[2]	1500°C (2732°F)	30,200	3,910	1,460	846	681
Sillimanite[2]	1500°C (2732°F)	46,700	36,300	11,500	4,290	3,150
Silica[2]	1500°C (2732°F)	77,500	49,000	15,700	8,050	5,660
Magnesite[2]	1500°C (2732°F)		4,780,000	94,700	2,790	615
Diaspore[2]	1500°C (2732°F)	35,000	2,920	886		
Bauxite brick[3]			17,200	6,100	2,200	1,100
Carborundum brick[3] (recrystallized)			4.1	2 5	1.7	1.6
Carborundum brick[3] (10 per cent clay bond)			197,000	29,500	10,000	8,590
Chrome brick[3]			171	63	85	41
Fireclay brick[4]			10,800	4,160	1,420	890
Fireclay brick[5]				480,000	180,000	80,000
Fireclay brick[6]				2,300	690	280
Fireclay brick[6]			50,000	50,000	15,000	3,000
Magnesite brick[2]			708,000	193,000	22,400	2,500
Magnesite brick[3]				100,000	40,000	3,000
Magnesite brick[7]				12,000	400	
Kaolin brick[6]				50,000	15,000	3,000
Silica brick[3]			300,000	62,000	16,500	8,420
Silica brick[4]				360,000	125,000	63,000
Silica brick[5]					2,400	710
Zirconia brick[8]			131,300	1,230		
Zirconia brick[9]				1,250	300	
Zirconia brick[3]				7,710	968	412

[1] King.
[2] Henry.
[3] Hartman.
[4] Wilkes.
[5] Stansfield, *et al.*
[6] Babcock & Wilcox Laboratory.
[7] Northrup.
[8] Nernst and Reynolds.
[9] Arnold.

At low temperatures, refractories conduct very slightly. As the temperature is raised, the conductivity increases rapidly until the melting point is reached, where electrolytic conduction occurs. With a pure material, the conduction would be low up to the melting point; but with the average refractory, liquid phases are formed by the impurities at relatively low temperatures, so that we get an early falling off of the resistance. In general, a pure, high-melting-point material will give the best high-temperature, electrical resistivity.

Part IV
USE

CHAPTER XXI

REFRACTORIES IN THE IRON AND STEEL INDUSTRY

1. Introduction. *Dependence of the Industry on Refractories.* The iron and steel industry is so dependent on refractories for efficient production that all the larger steel companies are themselves conducting research on refractories or are cooperating with the refractory manufacturers to obtain the best product for each position in the furnace. Unquestionably, in many cases, refractories capable of withstanding higher temperatures would permit more efficient production of steel and often a better quality of steel. For that reason, a great deal of effort is being expended on the study of high-temperature refractories, particularly for the open-hearth furnace.

Future Development. A problem that requires solution in the future is the production for the open-hearth furnace of a roof brick capable of operating at 100 or 200° higher than the silica roof and still giving a satisfactory life. The economy of insulation is now being thoroughly appreciated in the iron and steel industry, and to accompany insulation we must have a better quality lining brick to stand the greater mean temperature imposed. The super-duty silica brick is a step in this direction, and the experiments on the basic roof are watched with interest. In the heat-treating field, the development of lightweight refractories has been advancing rapidly, and now the insulating firebrick is almost exclusively used. The possibility of making sectional furnaces of portable panels that can be built around the completely fabricated structure for heat treating is being rapidly developed. Carbon refractories will undoubtedly receive increased study, particularly in the blast furnaces.

The disintegration of refractories under reducing conditions must receive more study, and bricks capable of withstanding this deteriorating influence more successfully will undoubtedly be developed.

2. Blast Furnace. *Principles of Operation.* The blast furnace is the primary unit for reducing iron ore to iron. The charge, which is a mixture of iron ore, limestone and coke, is blasted with preheated air in the correct amount to generate heat and form carbon monoxide, which reduces the ore to melted iron and slag. The composition of the iron depends a great deal on the type of ore used, but control of the final composition is possible in the blast furnace itself, except for manganese and phosphorus which cannot be greatly varied.

put into operation in this country. Although it is too early to evaluate these refractories completely, they certainly look promising. It is stated that in England a furnace is being tried with the carbon blocks above the slag line, where it is expected that the reducing atmosphere will protect them. Russia, also, seems to be using carbon linings. We have, as yet, no answer as to the relative merits of the block lining and the rammed lining; but in a few years, enough experience should be had with both to give a positive indication. The details of a German carbon-block-lined furnace are given by Seil.[93]

The bricks in the shaft of the furnace need not be so refractory as those in the lower part because the temperature decreases to approximately 400° at the exit. However, the bricks should be hard and resistant to the abrasion of the moving charge; and most important of all, they should be stable under the disintegrating effect of carbon monoxide, which was discussed more fully in Chap. XVI. It is generally believed that if the iron in the bricks has been converted to iron silicate by high firing, little disintegration will occur. The shaft bricks also are subject to disintegration in the upper portions from metallic zinc, which is sometimes reduced from the ore and, volatilizing, settles in the cooler portions of the lining, causing swelling and disintegration. Alkalies that are vaporized in the lower sections of the furnace also condense in the cooler parts and decrease the life of the lining.

Life of Refractories. The nature of the blast furnace is such that little or no repairing can be done on the structure during a campaign, and therefore the life of the weakest part of the structure determines the total life. Usually the furnace must be shut down because of wearing away of the wall somewhere in the shaft due to slag erosion and abrasion. When the wall becomes so thin that the temperature on the outside casing cannot be held down even by extra cooling, it is impossible to continue the furnace in operation. The modern furnace with thorough water cooling gives excellent life, and campaigns of 3 to 5 years are commonly reported. In general, it would seem that the refractories available for the blast furnace are satisfactory for their purpose, but perhaps higher densities for the brick in the lower part of the furnace can still be achieved by more careful sizing of the raw materials, vacuum treatment, and higher pressures. Higher firing of the brick in the shaft will make them more stable in regard to disintegrating influences, but many problems still need study as far as these factors are concerned.

In Fig. 329 are shown[9] the wear lines in a blast furnace at the end of a campaign. The first zone of wear is at the top under the stock-line wear plates and is due mainly to abrasion. The second zone is above the mantle and is caused by disintegrating influences of carbon monoxide, alkalies, and zinc, as well as slag erosion.

The checkers in the stoves show gradual deterioration due to slumping and shifting, but accurate pyrometer control to prevent overheating will minimize this condition. The use of super-duty fireclay brick in the upper portions of the checkers is generally recommended.

Table 111 gives an idea of the conditions encountered in the blast furnace.

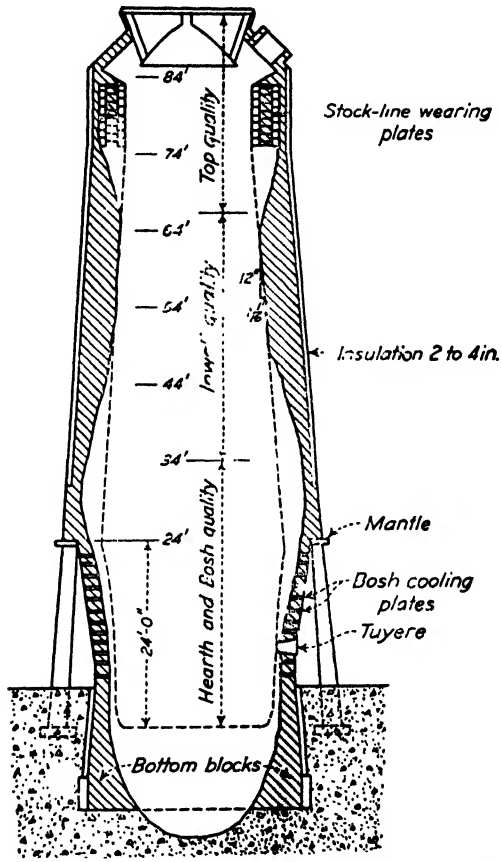


FIG. 329. Burn-out lines of furnace. (*Courtesy of W. R. McLain, Bull. Am. Ceram. Soc.*)

Two new developments in blast-furnace operation may have an important influence on the life of the lining. One of these is the use of oxygen-enriched air,[104,105] and the other, high pressure in the shaft. The latter method seems economically sound at present and should materially increase the capacity of a given furnace.

3. Cupola. *Principle of Operation.* The cupola is strictly a melting furnace using as a charge cast iron in the form of pigs, stove plate, and other

TABLE 111. ANALYSIS OF SERVICE CONDITIONS IN THE BLAST FURNACE

Furnace Part	Material	Temperature, °F.	Slagging action	Abrasion	Load, lb. per sq. in.	Spalling	Life, years	Remarks
Top	Dense low-heat-duty fireclay brick	400–600	None	Severe	Unimportant	Unimportant	3–5	
Upper inwall	Dense intermediate-duty fireclay brick	600–1000	Slight	Medium	Unimportant	Unimportant	3–5	
Lower inwall	Dense high-heat-duty fireclay brick	1000–2000	Considerable	Slight	10–15	Unimportant	3–5	Disintegration by CO, Zn, and alkalies
Bosh	Dense high-heat-duty fireclay brick	2000–3300	Severe	Slight	20–30	Unimportant	3–5	Water-cooling plates to protect refractory from slagging
Hearth	Dense high-heat-duty fireclay blocks. Also carbon blocks	2500–2900	Severe	None	May be high	Unimportant	3–5	Water-cooled jacket

scrap cast iron and in some cases scrap steel. The charge is alternately metal, coke, and some limestone as a flux. In a well-operated cupola, roughly 8 to 12 tons of iron can be melted to 1 ton of coke. The cupola

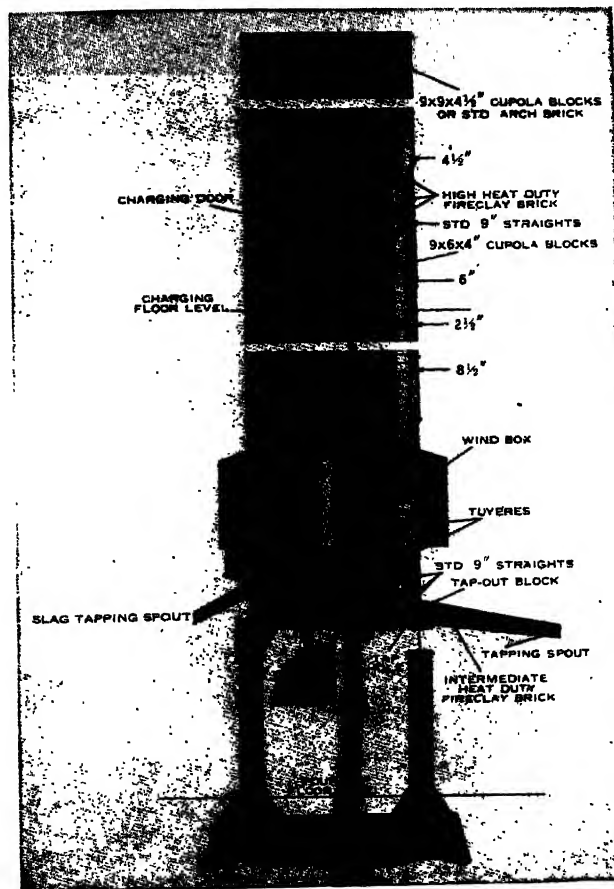


FIG. 330. Section of typical cupola. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

itself is quite similar to the blast furnace in shape, consisting of a hollow shaft with a charge entering through a door near the top and the molten iron being tapped out periodically or constantly at the bottom. Air for combustion enters the lower part of the shaft through tuyères in the same

way as for the blast furnace, but seldom is preheated air used in cupola melting. Unlike the blast furnace, the cupola is not used on continuous operation but is dumped each evening, repaired by patching, and started up the next day.

Typical Furnace. In Fig. 330 is shown a cross section of a typical cupola for melting away gray iron for foundry use. The shaft is completely lined with fireclay blocks molded to fit the curvature of the cupola. The door for charging is near the top of the shaft, and no attempt is made to collect the hot gases from the top. In the bottom of the shaft is a crucible for collecting molten iron, as clearly shown, together with the tap hole for draining off the melted iron. The bottom of the cupola can be dropped down at the end of a run for quicker cooling and easier repairs.

Types of Refractory Used. The refractories used in the cupola are fireclay blocks made with a dense structure by hard pressing or by dcairing. Considerable improvement has been made in the cupola refractory in the last few years in the way of a more uniform and denser structure. Such a structure is more capable of withstanding the abrasion and slagging; but on the other hand, because of the sudden temperature changes, the block must also have considerable resistance to spalling. Although the complete lining of the cupola lasts for a considerable length of time, perhaps for a year or more, it is necessary to make rather extensive repairs to the portion of the shaft around the tuyères every day by the addition of new blocks or simply by patching with a plastic material, which is usually made of crushed ganister and plastic fireclay.

Attempts have been made to line cupolas with a castable refractory consisting of grog, ganister, and high-alumina cement. Although this mixture has been used for patching in this country, the use of complete linings of this material has been confined in the past to European practice. Rammed linings are also used abroad because of their low cost. In Table 112 are given some of the conditions encountered by the refractory.

4. Open-hearth Furnace. *Principles of Operation.* The open-hearth furnace is a reverberatory type with a flame playing over a relatively shallow layer of metal. The charge may be pig iron, either solid or in the molten state directly from the blast furnace; most generally pig iron and scrap; or scrap and carbon. The reactions occurring in this furnace are mainly an oxidation of the carbon, elimination of the phosphorus in the basic process, and a decrease in the silicon, manganese, and sulfur. In the acid process (siliceous slag), it is impossible to eliminate the phosphorus; accordingly, only low-phosphorus materials can be used, which in this country limits the production of acid open-hearth steel to about 5 per cent of the total. For this reason, only the basic process will be considered here.

TABLE 112. ANALYSIS OF SERVICE CONDITIONS IN THE CUPOLA

Furnace part	Material	Temperature, °F	Slagging action	Abrasion	Load	Spalling	Life	Remarks
Shaft lining, upper..	High-heat-duty fireclay blocks, 9 × 6 × 4 in.	500–2000	None	Severe	Light	Important	1 year	
Shaft lining, lower..	High-heat-duty fireclay blocks 9 × 6 × 4 in.	2000–3000	Severe		Medium	Slight	1 year	Patching required every heat
Bottom..	Rammed sand and clay	2900	Severe		May be important	None	1 heat	
Tapping-spout lining.	Intermediate-heat-duty bricks	2600–2800	Slight	Cutting by metal	None	Severe	20–30 heats	

The output of the open-hearth furnace is mostly used for casting steel ingots, which are later rolled, hammered, or pressed into the desired shapes.

The fuel used in the open hearth is most commonly producer gas, but furnaces are fired by natural gas, fuel oil, tar, coke-oven gas, and even pulverized coal. The type of fuel governs the design of ports in the furnace and has a considerable influence on the life of the refractories. For example, producer gas gives a long flame that has a tendency to heat the end walls and downtakes, whereas the coke oven gas has a hot flame that tends to heat the roof near the burner end of the furnace. All open-hearth furnaces are of the regenerative type, in which the outgoing gases heat checker chambers. After a period of time, the flow is reversed and the incoming air and gas are preheated by passing through these hot chambers and then combined at the ports to form the combustion flame. Neither coke-oven nor natural gas can be preheated because of the tendency to crack.

Typical Furnace. In Fig. 331 is shown a cross section of a typical stationary 100-ton basic furnace, which is an average size. Most of the furnaces are of the stationary type, but a few tilt on a horizontal axis for pouring and to make up the back wall. The tilting makes the operation of the furnace somewhat simpler, but the initial cost is much greater, and there is some difficulty in making the air and gas connections tight. If anyone is interested in more detailed construction of the open-hearth furnace, he should refer to the excellent book by Buell.[38]

The hearth of the furnace is built up on steel plates, as shown in Fig. 331, with a layer of insulating brick, magnesite or chrome bricks, or a rammed mixture and then a fritted magnesite bottom, which is constantly being repaired during the campaign to maintain its normal thickness. The front and back walls of the furnace are usually made of silica brick with burned magnesite brick in the lower courses; but recently, chemically bonded brick of magnesite and metal-cased magnesite brick have been successfully used. A layer of chrome brick is usually introduced between the silica and magnesite brick.

Recently a considerable saving in time has been achieved by using rammed bottoms rather than fritting in a bottom in layers.[90]

The end walls and bulkheads are built up of silica, magnesite, or chrome brick; but here again, the metal-case brick have proved quite satisfactory in many installations. The ports are usually constructed of silica brick, but chrome and magnesite brick are used to withstand the slag and cutting action of the high-velocity dust-laden gases. Chromite ramming mixtures are sometimes used over the silica brick.

The doors of the furnace usually have water-cooled frames, which protect the brickwork from the mechanical abuse of the charging machine and give sufficient cooling to prevent deterioration of the front wall—a difficult portion of the furnace to repair.

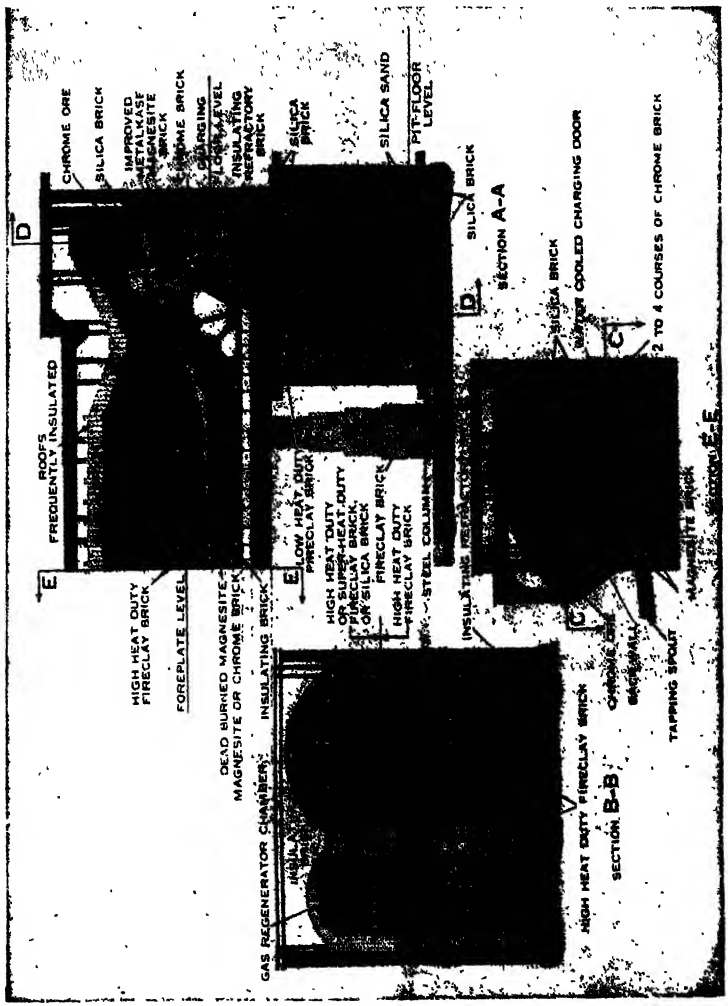


FIG. 331. Sections of typical basic open-hearth furnace. (*Courtesy of Harbison-Walker Refractories Company.*)

The roof of the open-hearth furnace is one of the most important portions of the structure, because the life of the furnace as a whole is more or less determined by the life of the roof. Generally, the refractories used in the sprung arch of the roof are silica brick of 13½ or 18 in. thick-

ness. As the temperature required to maintain a low-carbon steel for pouring is 1585°C (about 2880°F) and the temperature at which the silica brick in contact with iron oxide begins to soften is 1650°C (about 3000°F),[59] it will be seen that only a small operating interval is available and that for this reason, the temperature control must be carefully maintained. In the modern plants, the roof temperature is read with optical pyrometers; and in some cases, temperature controllers operating on a radiation-pyrometer principle are permanently installed to cut off the fuel whenever the temperature exceeds the upper limit.

It might be thought that the silica brick, because of its tendency to spall, would be unsatisfactory in a regenerative furnace where a periodic change in temperature occurs at each reversal. However, if one would examine the expansion curve of a silica brick as shown in Fig. 297 of Chap. XVII, it will be noticed that above the red-heat range, the volume of the brick is substantially constant and changes in temperature in the higher zones will cause no appreciable volume change. In other words, the silica brick is unexcelled for these particular conditions, and this constant volume at high temperatures explains why such good results are obtained with them.

Steel manufacturers have long desired a roof brick with a higher temperature range than silica, because it is obvious that if the open hearth could run at 200 or 300°F higher temperature, production from a given unit could be greatly increased and, at the same time, qualities of steel that now can be produced only in the electric furnace could be turned out more cheaply in the open hearth. For this reason, a great deal of experimentation has been taking place both in this country and abroad on the use of more refractory materials. In Germany, specially made magnesite brick[58] have been used with greater resistance to spalling than the usual type, accomplished by special treatment to give a maximum flexibility to the structure.[35] Specially treated chrome brick have been used in the roof of the open hearth; and more recently, bricks made of mixtures of chrome and magnesite have seen extensive trials, particularly in England. The results from these refractories, when analyzed, do not give us as yet any clear picture of the possibilities in this direction because even though a number of successful trials have been reported, this construction has not been adopted at all extensively, since the much greater cost of the roof as compared with silica does not seem to be justified.

In spite of this, several basic roofs have been put in operation in this country and Canada, but further improvement of the brick is needed before they will compete seriously with silica brick in our type of operation. The recent German success with the basic roof depends, as

explained by Seil,[93] largely on their practice of using a high percentage of hot metal (about 70 per cent), so the heat shock is not great in charging.

The super-duty silica brick of more than usually pure ganister has shown considerable promise in permitting somewhat higher roof temperatures, but not all melters agree on its superiority over the standard silica brick.

The downtakes to the checker chambers are usually lined with silica brick, as is the upper part of the checker chamber itself. The checkers usually consist of hard-burned fireclay blocks such as $9 \times 6 \times 3$ or $10\frac{1}{2} \times 4\frac{1}{2} \times 4\frac{1}{2}$ in. in size. Often, however, the upper courses are made of silica because of the higher temperature conditions. A great many different types of checker block have been suggested and tried, and much theoretical work has been given over to the consideration of the checker efficiency. Many of these are noted in the references.[52,53,60] The fact remains, however, that most of the furnaces now built use the simple, rectangular checker block. The life of the furnace, in some cases, depends on the checkers, because as the campaign continues, the checker passages decrease as a result of building up of slag on the checkers, collection of dust in the passages, and spalling off of fragments of the checker bricks themselves, which fall down and tend to plug the passages. It is usual to design the checkers to give a life equal to or considerably longer than that of the furnace roof without too great loss in regenerative efficiency. Anyone interested in more detailed construction of the checker design should again refer to Buell.

The cost of commercial oxygen has been so reduced by modern methods ($20 to $40 per ton) that enrichment of the combustion air is feasible with more rapid melting.[102,104,105] Griffith[73] gives some figure to show a saving of about 2 hr in total heat time and, in addition, a real saving in fuel. It is believed that oxygen may be generally used in the future, and this will impose more problems on the refractories manufacturers.

Life of the Refractories. In Table 113 is given a résumé of the service conditions and life of the refractories in various parts of the basic open-hearth furnace. It should be realized that the figures given in this table are more or less average figures and that many exceptions will be found under particular conditions. All that it is hoped to do is to give a general picture that will explain why certain types of refractory are used and what the possibilities are of finding an improved material for that particular service.

5. Pouring-pit Refractories. *Ladles.* The steel ladle is used to receive the molten steel from the open-hearth furnace. In the ladle, the steel may receive some treatment such as the addition of deoxidizers or alloying elements, after which it is teemed into the ingot molds through a

TABLE 113. ANALYSIS OF SERVICE CONDITIONS IN PRODUCER-GAS-FIRED STATIONARY OPEN-HEARTH FURNACE
(Adapted from Industrial Survey of Conditions Surrounding Refractory Service in Open Hearth Practice, "Manual of ASTM Standards on Refractory Materials")

Furnace part	Material	Temperature	Slagging action	Abrasion	Load, lb per sq. in.	Spalling	Life	Remarks
Hearth:								
Bottom	Magnesite	Up to 3000°F. (1650°C.)	Severe	Severe	Unimportant	None	20 years	Development of cracks allows infiltration of metal, causing disruption of bottom
Banks	Dead-burned magnesite and dolomite	Up to 3000°F. (1650°C.)	Moderate	Severe	10 max.	None		
Front wall	Silica brick	Up to 3000°F. (1650°C.)	Severe	Unimportant	10 max.	Important		There may be considerable spalling in roof and walls if furnace is heated too rapidly
	Chrome brick	Down to 1200°F. (650°C.)						
Back wall	Silica brick	Up to 3000°F. (1650°C.)	Severe	Severe in some furnaces	10 max.	Usually slight		
	Chrome brick Magnesite brick	Down to 1200°F. (650°C.)						
Roof	Silica brick*	Up to 3000°F. (1650°C.) Down to 1200°F (650°C.)	Severe	Unimportant	Arch stresses	Important	250–500 heats	
Ports	Silica brick	Up to 3000°F. (1650°C) Down to 2000°F. (1095°C)	Severe	Important	Unimportant	Usually slight		
Bulkhead(endwall)	Silica brick Chrome brick Magnesite brick†	2900°F. (1595°C.), max. 2000°F. (1095°C.), min.	Severe	Important	10 to 15	Slight usually except on repairs	100–300 heats	
Downtake	Silica brick	2900°F. (1595°C.), max. 2000°F. (1095°C.), min.	Severe	Moderate	15 to 20	Slight		
Slag pocket	Silica brick	2900°F (1595°C.), max. 2000°F (1095°C), min.	Severe	Unimportant	5 to 10	Unimportant		

* Magnesite and chrome-magnesite brick have been used.

† Metal-case brick often used.

TABLE 113. ANALYSIS OF SERVICE CONDITIONS IN PRODUCER-GAS-FIRED STATIONARY OPEN-HEARTH FURNACE (*Continued*)

Furnace part	Material	Temperature	Slagging action	Abrasion	Load, lb per sq. in.	Spalling	Life	Remarks
Upper checkers	High-heat-duty fireclay brick Silica brick	Gas: 2400°F. (1315°C.), max 1100°F (595°C.), min. Air: 2600°F. (1425°C.), max. 250°F. (120°C.), min.	Important at top; not important at bottom	Slight except in upper portion	5 to 15	Usually slight		Gas checkers: Top varies from 2400 to 2000°F. (1315 to 1095°C.); bottom from 1100 to 1400°F. (595 to 760°C.) Air checkers: Top varies from 2600 to 2000°F. (1425 to 1095°C.); bottom from 250 to 1400°F. (120 to 760°C.)
Lower checkers Checker chambers	High-heat-duty fireclay brick	Same as for "Upper checkers"	Same as for "Upper checkers"	Same as for "Upper checkers"	10 to 20	Usually slight		
Flue to stack	Intermediate-heat-duty fireclay brick	Up to 1350°F. (730°C.)	Unimportant	Unimportant	Unimportant	None		
Stack	Intermediate- and moderate-heat duty fireclay brick	Up to 1200°F. (650°C.) at bottom stack	Unimportant	Unimportant	Unimportant because of low temperature	None		

nozzle and stopper in the bottom of the ladle. The refractories used to line the ladle present a real problem because they must fulfill the following requirements:

1. Good resistance to temperature shock due to the sudden heating when the molten steel is poured into the ladle.
2. Good resistance to the slag layer on top of the steel.
3. Resistance to abrasion of the molten steel.
4. Freedom from particles of the refractory mixing in the molten steel and forming inclusions.
5. Low thermal conductivity to prevent the formation of sculls.
6. Tight joints to prevent adhesion of the sculls to the bottom and sides of the ladle.

As the steel is generally made in a basic furnace, it would seem reasonable that the lining of the ladle should also be basic; but unfortunately, a basic material cannot be found that would stand the sudden temperature change of pouring without serious failure. Therefore, it has been thought necessary to make the ladle lining out of fireclay brick with a fine-grained, fairly dense structure yet sufficiently porous to give good spalling resistance. There have been two schools of thought on ladle bricks: one advocating a high-silica brick of comparatively low fusion point which actually glazes over slightly on the surface and provides a smooth inner lining. The other type of brick recommended is the high-alumina brick of flint clay or diaspore having high refractoriness. Both types of brick are used in ladles; but as yet, no definite conclusion can be drawn as to the best type. When it is realized that perhaps 15 or 20 heats is the average for the ladle lining, possibilities of real improvement in the refractories are evident.

It is obvious that if care is taken to preheat the ladle to a high temperature and then use it continuously, the basic lining should be very satisfactory. This is shown by some results in France, where a basic ladle was used for 30,000 heats. Not only does the basic lining give a long life, but it is so resistant that the steel is not contaminated with nonmetallic inclusions. The basic lining should receive more serious thought in this country.

In lining a ladle, the common practice is to use a thickness of 2½ to 9 in., depending on the size of the ladle, and modern usage seems to tend toward the use of 1 or 1½ in. of insulation between the refractory lining and the steel shell. The ladle bricks, usually in two layers, should be uniform in size so that the thinnest possible dipped joints can be made. Care is necessary in drying out the ladle before use, which is usually done by building a fire of wood or coke in the bottom of the ladle or introducing gas burners. Practice varies in the time required for drying, some ladles being dried out in as short as 8 hr, and some in 48 hr. The life of the

ladle lining depends to some extent on the type of steel, certain alloys being much more severe on the lining than carbon steel. Fluorspar, which is often used to increase the fluidity of the flux, has a severe action on the ladle lining and will often materially decrease its life. Smaller ladles for cast iron are often lined with a fireclay plastic that must vitrify and give a hard surface.

Nozzles, Stoppers, and Sleeves. The nozzle used in teeming steel from the ladle is a very important part of the ladle. A cross section of a typical nozzle and stopper assembly is shown in Fig. 332. A good stopper and nozzle should give a clean flow of steel without spattering at a substantially constant rate throughout the pouring operation, should be able to shut off the stream between ingot molds cleanly without dribbling, and it should be possible to open the nozzle on the first ingot without sticking.

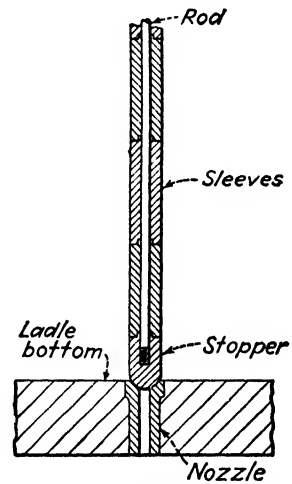


FIG. 332. Nozzle and stopper assembly.

In order to get a uniform rate of flow from the ladle, a material that will slowly erode and increase the diameter during the pouring operation must be used in the nozzle. It has been found that fireclay nozzles will have this property of giving a comparatively uniform flow rate from the beginning to the end of the pouring. On the other hand, a nozzle of magnesite is so resistant to erosion that it maintains substantially a constant diameter and therefore the rate of flow decreases, as shown in Fig. 333.

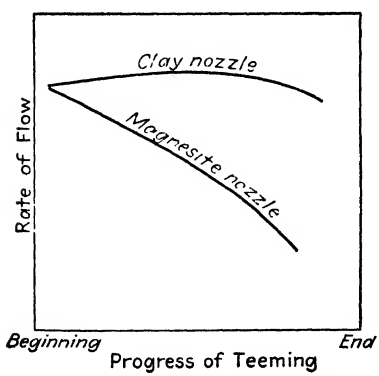


FIG. 333. Flow of steel through nozzles.

In order to get a tight fit between the nozzle and stopper, it is usually desirable to have one of them slightly plastic, but not both, or sticking is certain to result. For this reason, either the nozzle or the stopper will generally be made of a more refractory clay than the other; or in many cases, the stopper would be made of graphite and clay, which are more rigid at the pouring temperature than the clay alone.

The steel rod attached to the stopper must pass down through the molten steel in the ladle and therefore must be protected with refractory sleeves. They are made of a fireclay, and it is particularly important

that they resist cracking under the sudden heat shock. It is also important that the joints between the sleeves be carefully fitted so that the molten steel cannot force them apart.

In recent years, a great deal of interest has been shown in steel inclusions. It is beginning to be realized that many of these are due to particles of refractory from the ladle lining or from the nozzle and that the ability to produce really clean steel would seem to depend largely on finding a refractory that would be more stable than the fireclay refractory now used.

Tap Holes. The tap hole in the open-hearth furnace must consist of a material strong enough to hold the pressure of the molten steel without breaking out and, at the same time, sufficiently soft to be knocked out with the tapping bar. It is general practice to make up a mixture of raw and burned dolomite for this purpose, although in some cases chrome-base cements have been used.

Hot Tops and Plugs. The plugs are used at the bottom of certain ingot molds to receive the direct impact of the stream of molten steel from the ladle. They must, therefore, be resistant to spalling and at the same time sufficiently dense to prevent erosion. They are usually made of a fireclay of comparatively low refractoriness and generally give little trouble.

The hot tops are placed on top of the ingot mold to prevent too rapid solidification of the top of the ingot and consequently a deep pipe. The hot tops must have a sufficiently close structure so that the steel will not penetrate them, and yet it is desirable to have them of light weight for low specific heat and low thermal conductivity with, at the same time, good spalling resistance. As they are generally used only once, the cost must be low. Usually, a comparatively low-burned fireclay mix is used, but some success has been had with lightweight refractories coated with a material to prevent penetration of the steel into the pores.

6. Air Furnace. *Principles of Operation.* The production of malleable iron is generally carried out in the air furnace. The malleable iron is produced from mixtures of pig iron, steel, and malleable foundry scrap, which is refined in the furnace to produce the proper percentages of carbon, silicon, sulfur, manganese, and phosphorus. When the malleable iron is first cast, it has practically all the carbon in the form of carbide of iron, which gives a comparatively brittle structure. The cast objects are then subjected to a heat-treating process while packed in iron boxes, perhaps seven or eight deep, for a considerable length of time, after which the carbon is precipitated and gathers into regular nodules known as "temper carbon." Sometimes the castings are simply annealed without packing. In the final condition, the metal is ductile and malleable and shows considerable elongation.

Typical Air Furnace. Figure 334 shows a section of a typical air furnace, which consists of a shallow hearth made of silica sand and a firebrick wall and crown to cover it. An average-size hearth is 6 by 20 ft

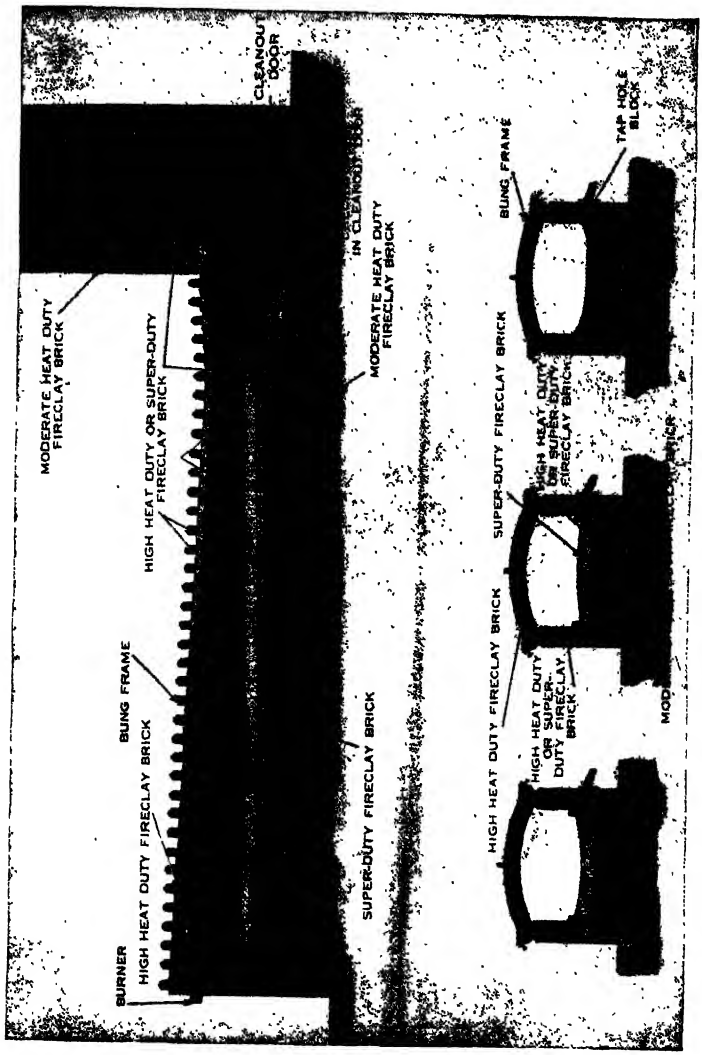


FIG. 334. Pulverized coal-fired reverberatory furnace for malleable iron. (*Courtesy of Harbison-Walker Refractories Company.*)

with a capacity of 15 tons, but furnaces up to 50-ton capacity have been made. Unlike most reverberatory furnaces, the crown is not fixed but is composed of separate bungs in which a ring of bricks comprising a section of the arch is clamped in an iron framework. In this way, one

TABLE 114. CLASSIFICATION OF REFRACTORIES FOR MALLEABLE-IRON INDUSTRY

(Adapted from Industrial Survey of Conditions Surrounding Refractory Service in the Malleable-iron Industry, "Manual of ASTM Standards on Refractory Materials")

	Part (see Fig. 334)	Material	Temperature	Spalling	Slagging	Load	Abrasion	Life	Remarks
Air furnace	Bungs	Fireclay brick	Up to 3000°F. (1650°C.)	Very important where bungs removed for charging immediately after tapping	Minor importance	See note under "Remarks"	Important near back bridge wall	20–30 heats	The brick in the bungs are subjected to pressure that may be as high as 1000 lb. per sq. in. owing to setting up the clamps too tightly. This would be increased considerably as a result of thermal expansion when the bungs were heated up
	Side walls	Fireclay brick	From 3000°F. (1650°C.) at front to 2400°F. (1315°C.) at back	Important above the slag line	Important from the hearth up to the slag line	10 lb. per sq. in. max.	Unimportant		
	Bottom	Fireclay brick or silica sand	Varies from plant to plant and stage of melting operation. Approximately that of the metal	Minor importance	Important especially in "Duplexing"	Minor importance	Important		

	Part (see Fig 334)	Material	Temperature	Spalling	Slagging	Load	Abrasion	Life	Remarks
	Stack lining	Fireclay brick	2400°F. (1315°C.) max.	Unimportant	Unimportant	Depends upon construction. 50 lb. per sq in. max. Usually an inner lining is built to a height of 15 to 20 ft. The load here is not in excess of 15 lb. per sq. in	Unimportant		
	Waste heat boilers	Fireclay brick	2400 to 2600°F. (1315 to 1425°C.)	Moderate	Unimportant	Unimportant	Unimportant		
	Air preheaters	Fireclay brick	2400 to 2600°F. (1315 to 1425°C.)	Moderate	Unimportant	Unimportant	Unimportant		
Annealing oven	Combustion chamber	Fireclay brick See note under "Remarks"	2100°F. (1150°C.) See note under "Remarks"	Moderate	Moderate	Unimportant	Unimportant		Some continuous ovens are oil-fired and higher temperatures prevail particularly in the bridge wall. Superduty fireclay brick, high-alumina brick, and silica brick are then used
	Doors	Fireclay brick or insulating refractories	1600 to 1800°F. (870 to 980°C.)	Unimportant	Unimportant	Unimportant	Unimportant		
	Walls	Fireclay brick or insulating refractories	1600 to 1800°F. (870 to 980°C.)	Unimportant	Unimportant	15 lb. per sq in. max.	Unimportant		

or more bungs can be lifted from the furnace at any time with a crane and the furnace charged through the opening thus produced. The fuel used for heating this type of furnace may be coal, oil, or gas, but powdered fuel is, perhaps, most used. This produces rapid heating and comparatively high temperatures; consequently the crown of the furnace receives considerable abuse. A furnace is brought up to heat in 1½ hr and held 5 to 8 hr. The bungs have a comparatively short life of 20 to 30 heats as a result of the rapid heating and cooling, but the side and end walls give generally good service. In Table 114 is given a summary of the service conditions in the air furnace.

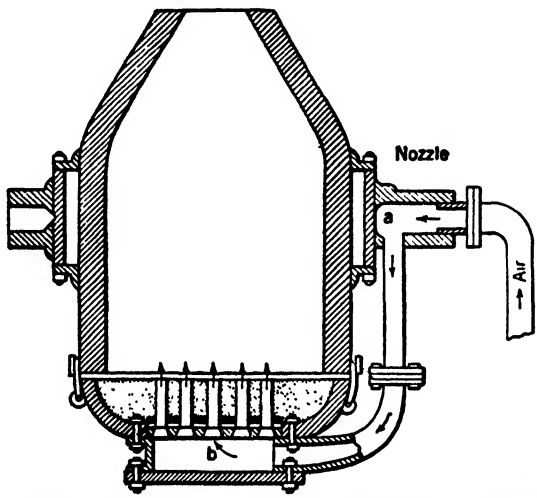


FIG. 335. Bessemer converter. (*From "Iron and Steel," by H. M. Boylston.*)

7. Bessemer Converter. *Construction and Operation.* The Bessemer converter is a pear-shaped, refractory-lined vessel on trunnions, which permit it to be tilted from the horizontal to the vertical position. The bottom consists of a refractory containing a large number of holes through which air can be blown under considerable pressure. A typical converter is shown in Fig. 335.

In operation, the converter while on its side is charged with molten iron from the mixer or blast furnace. It is then rocked into an upright position after the air blast has been applied, thus forcing air up through the molten metal and oxidizing the carbon and silicon to bring it down to the right composition. Experiments are being made on the use of oxygen-enriched air for the blast, which may well alter the conditions for the refractory.

Type of Refractory Used. Most of the converters are acid lined with silica brick or natural furnace stone such as sandstone or mica schist. The bottoms of the converter are usually made of fireclay and must be frequently replaced, as 10 to 30 heats is the average life. The walls of the converter, however, may give a life of 200 or 300 heats before extensive replacements are necessary.

8. Electric-arc Furnaces. *Principle of Operation.* Furnaces of this type are used to melt iron and steel by the heat of an arc formed between the slag layer and the overhead electrodes, usually three in number, which can be raised and lowered to accommodate the changes in metal height and loss in electrode length. There are many variations in types of furnace, but most of them consist of a cylindrical, refractory-lined shell with a domed roof and a charging door in the side. Nearly all of them are on trunnions so that they are poured by tilting.

The acid-type furnace is used mainly for steel castings and iron, whereas the basic furnace is most commonly used for production of steel ingots.

Construction. In Fig. 336 is shown a cross section of two typical electric basic furnaces. The bottom is composed of about 10 in. of rammed, dead-burned magnesite or electrically sintered magnesite, bonded with organic material or silica of soda. Such a bottom will probably be patched every heat but, under these conditions, will give good service.

The lower side walls are constructed of magnesite brick; and for this purpose, a low-iron magnesite is often preferred because of its better resistance to spalling. The upper side walls are usually made of silica brick.

The roof, which is in the form of a dome, is generally made of silica brick, using specially made shapes to fit around the electrodes. Good success has been obtained, however, with roof bricks of other materials such as super-duty fireclay, kaolin, and mullite, all of which are more resistant to spalling during the week-end shutdowns than the silica. An average roof will have a life of 100 to 150 heats, although a longer life is sometimes obtained.

9. High-frequency Induction Melting Furnaces. *Principle of Operation.* This type of furnace melts metal by inducing high currents in the charge by means of an external coil surrounding the crucible. This furnace differs from all others in that the heat is generated directly in the metal itself and the crucible is not subjected to any other heating. High-frequency induction furnaces are made in small units for experimental melts of a few pounds up to 5-ton steel-melting furnaces. This kind of melting has certain advantages, particularly for alloy steels, in that a thorough stirring of the melt takes place and the analysis of the resultant steel can be accurately controlled.

Refractories. In Fig. 337 is shown a cross section of a large high-frequency induction furnace for melting alloy steels. The high-frequency current is carried by the water-cooled coil, inside which is a formed mica sleeve or troweled on sillimanite mix for coil protection. On the inner

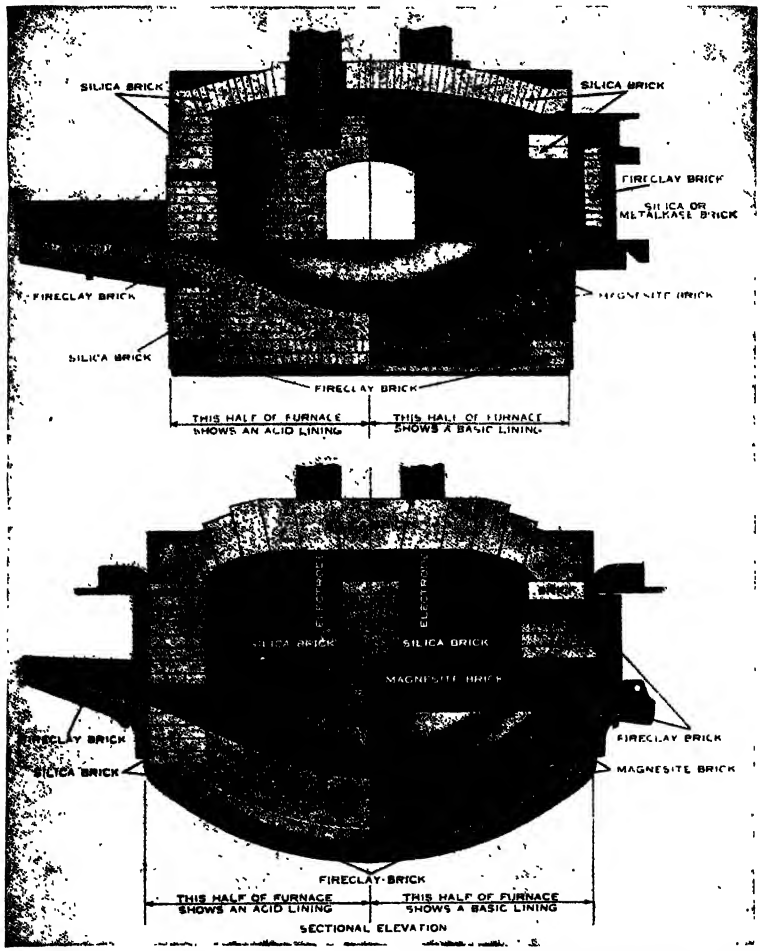


FIG. 336. Typical electric steel-melting furnaces. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

side of this is rammed a thin layer of refractory to form the melting chamber. For the highest efficiency, this refractory must be thin, and yet it must not crack during the melting operation. The preferred method of putting in this refractory is to ram it by hand inside a core made in the form of a steel or asbestos cylinder. The core can be withdrawn or

melted out while, at the same time, fritting the surface of the refractory together into a strong mass.

A satisfactory refractory may be a rammed ganister bonded with a little clay or silicate of soda for acid furnaces. Electrically sintered magnesite with an organic binder is used for basic furnaces, although linings are fritted in place with no bond by melting out an asbestos sleeve. With patching, 100 to 200 heats can be obtained with a single lining. Fused alumina and zircon have also been tried with good success in special cases.

For the smaller furnaces, prefired crucibles are generally used, magnesite being usually preferred.

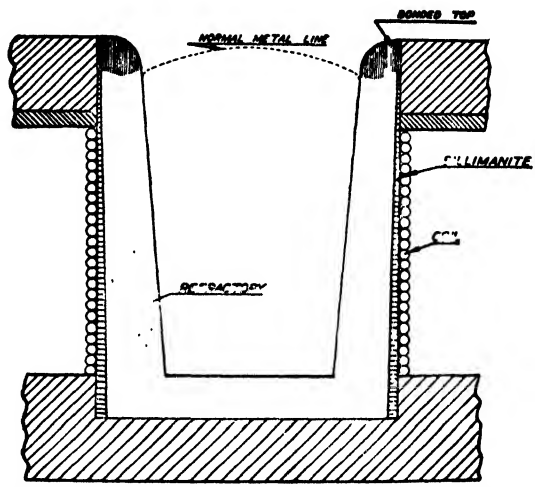


FIG. 337. General arrangement of coreless induction furnace. (*Courtesy of B. W. Magalis, Babcock & Wilcox Company.*)

10. Furnaces for Forming Operations. *Soaking Pits.* The soaking pit as shown in Fig. 338 consists of a rectangular or cylindrical furnace generally heated by tangential burners using either gas or oil as fuel. Regeneration is often employed. The removable cover, automatically operated, allows the heavy ingots to be placed or removed with an overhead crane.

The bottoms of these furnaces are made of rammed coke and molasses or rammed chrome plastic to withstand the action of mill scale, which forms in comparatively large quantities in furnaces of this type. The side walls are usually made of fireclay or silica brick, but unburned magnesite or chrome brick have been tried with success.

The cover is one of the most important parts of the furnace, as it must withstand considerable mechanical shock due to the frequent

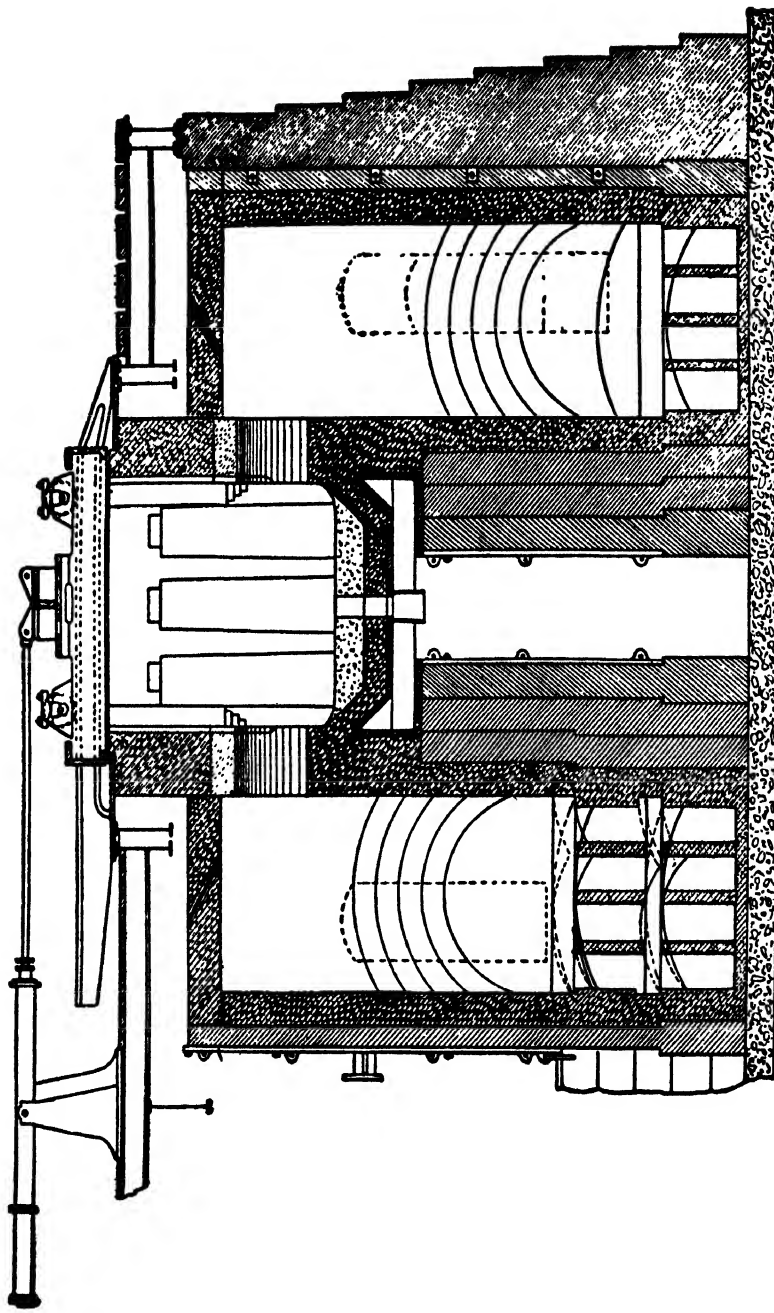


FIG. 338. Soaking pit. (*From "The Making, Shaping and Treating of Steel," Carnegie Steel Company.*)

opening and closing; and at the same time, it should be as light as possible for the quick operation necessary for efficiency. For this reason, covers have recently been made almost entirely from insulating firebrick, because it not only reduces the weight of the refractory in the cover but also permits much lighter steelwork to be employed. These refractories must be carefully selected so that they will stand the spalling conditions of frequent opening and closing of the cover, have a light weight and a good insulation value.

Billet-heating Furnaces. Billet-heating furnaces may be of the continuous type, a typical example of which is shown in Fig. 339. Here the billets pass through the furnace in a continuous layer on water-cooled rails and are heated mainly by convection of the hot combustion gases

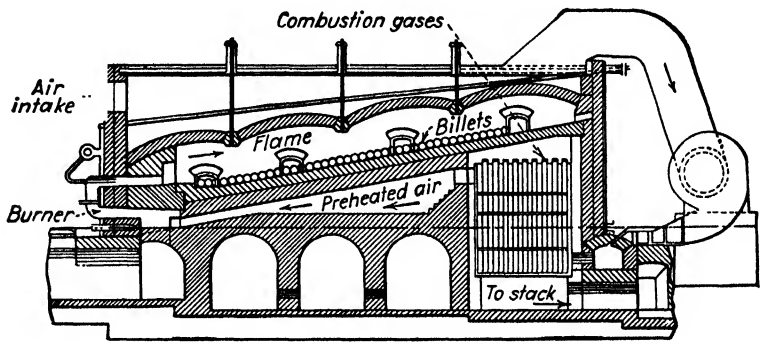


FIG. 339. Continuous billet-heating furnace.

passing over and under them. This type of furnace is a true recuperative type, due to the counterflow action, so that the efficiency is comparatively high. The hotter parts of the furnace are made of high-quality fireclay brick or kaolin brick, but the upper structure of the cooler portions is generally made from low-heat-duty brick with good insulation. The bottom of the furnace, which must resist the action of mill scale, is usually constructed of rammed chrome plastic at the hotter end.

Rotary-hearth billet-heating furnaces have many advantages, such as small floor space, ready handling of the billets, and good fuel consumption. They are replacing the horizontal type in many modern mills.

Batch-type billet-heating furnaces are constructed in a large number of designs, but here the bottom is usually made of chrome and the upper structure of insulating firebrick. The value of insulating firebrick is particularly evident in the doors, which are decreased in weight so that they can be operated more rapidly and with less discomfort to the workman.

Forging Furnaces. Forging furnaces are made in many types. The refractory used is generally of fireclay, but the use of lightweight refractories is becoming quite prevalent in modern construction. The floor of the furnace may be of dense fireclay brick or rammed chrome plastic.

11. Heat-treating and Stress-relieving Furnaces. Furnaces of this type are required to withstand only moderate temperatures. Heat-treating furnaces for high-speed steel might require a maximum temperature of 2400°F (about 1300°C), whereas stress-relieving furnaces would reach only 1400°F (about 760°C). For this reason, it has been found

FIG. 340. Large car bottom stress-relieving furnace. (*Courtesy of Babcock and Wilcox Company.*)

that the insulating firebrick can be used very successfully in many constructions. It has the advantage of giving a material saving in fuel, lower cost of burner equipment, and, in many cases, increased life.

In Fig. 340 is shown an illustration of a large car bottom stress-relieving furnace fired by natural gas which will take drums to 100 tons in weight. It is lined with insulating firebrick, thus giving a very uniform distribution of temperature as well as excellent fuel economy.

12. Bright Annealing Furnaces. Furnaces of this type operate with a controlled atmosphere, usually with hydrogen. The temperatures are low; and for this reason, the insulating firebrick has seen extensive use both in the continuous and in the intermittent types. Because of the strong reducing action of the hydrogen, it is necessary to employ a refrac-

tory that will be stable under these operating conditions. For that reason, bricks low in iron oxide content are desirable.

CHAPTER XXII

REFRACTORIES IN THE NONFERROUS-METAL INDUSTRY

1. Copper Production. *Outline of the Process.* The common copper ores contain between 1 and 2 per cent copper and must be concentrated by ore-dressing methods, which bring the percentage of copper up to between 20 and 30 per cent. If this concentrated ore contains free sulfur or a too high quantity of iron sulfide, it must be roasted to drive off a portion of the sulfur as SO_2. This roasting takes place at a low temperature in a multiple-hearth furnace (Fig. 341); and although no serious refractory problems are encountered here, the hearths of fireclay brick must be abrasion resistant. The roasted ore is then smelted, which is carried out at the present time in a reverberatory type of furnace, as the blast furnace is seldom used. In this operation, the copper sulfide is separated from the gangue and some of the iron as a matte, which is a mixture of copper and iron sulfide. This matte is then treated in a converter where air is blown through the melted sulfides, thus oxidizing the sulfur and the iron, the latter being taken up in the slag and the former passing out of the furnace as SO_2. The crude copper, called "blister copper," is then treated in an anode furnace where it is further oxidized, and the base metal oxides formed are taken up in the slag and removed. The copper is then reduced by covering with coke and introducing green poles which give off CO and water vapor, thus reducing all but a very small amount of the copper oxide to metallic copper. The copper from this process is cast in anodes and treated in a cell to form electrolytic copper cathodes; at the same time, the gold and silver can be recovered in the slimes. The electrolytic copper cathodes are then melted in a fining furnace and cast into commercial shapes.

Reverberatory Smelters. This type of furnace, as shown in Fig. 342, very much like a long open-hearth furnace, is fired at one end, usually with gas, oil, or powdered coal. The charge, which in the earlier furnaces was fed through openings in the center of the roof, is now fed through openings in the roof near the skewbacks. As the charge melts, it flows down to the cooler end of the furnace where the matte and slag can be tapped off separately. The size of these furnaces is usually 20 to 25 ft in width and 120 ft in length, capable of handling 500 to 1,000 tons of charge per day, although a few furnaces even larger than this have been constructed.

The bottom of the furnace is made of silica rammed in and fritted in place much in the same way as the acid bottom is put in an open hearth. The bottom must be sufficiently dense to prevent the penetration of the liquid matte and requires frequent repairs.

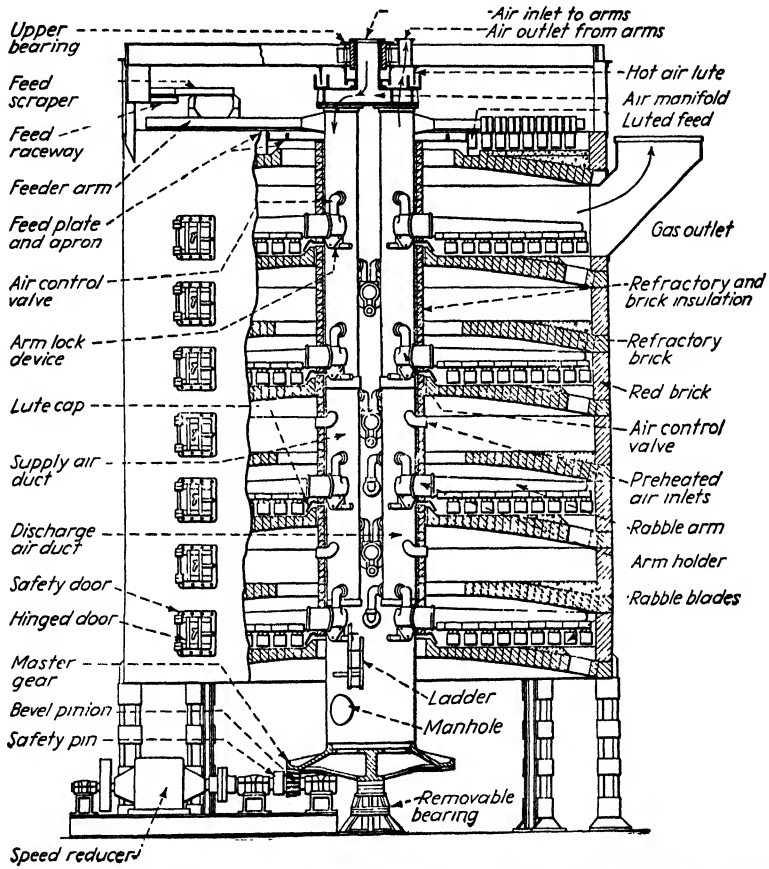


FIG. 341. Wedge roaster. (*Courtesy of Bethlehem Foundry and Machine Company, G. Thorpe.*)

The side walls of the furnace are generally silica brick, although magnesite brick have been used in the lower side walls. Water cooling at the burner end has been used in some furnaces; but at present, it is not common. Silica brick are also used in the end walls, but high-alumina brick have also been successful in some cases.

The roof of the reverberatory furnace is exposed to a great deal of dust, which fuses and produces a severe slag attack. Silica brick are generally used in the roof in spite of the fluxing effect. Within the last fifteen years,

magnesite brick either of the hard-fired, low-iron type or chemically bonded brick have been used quite extensively in the portion of the arch near the skewbacks, especially around the charging holes. Suspended roofs of chemically bonded magnesite have been tried with very good success in Canada. The life of the silica roof runs about 100 days; but with the use of magnesite, a somewhat longer life has been reported. Insulation of

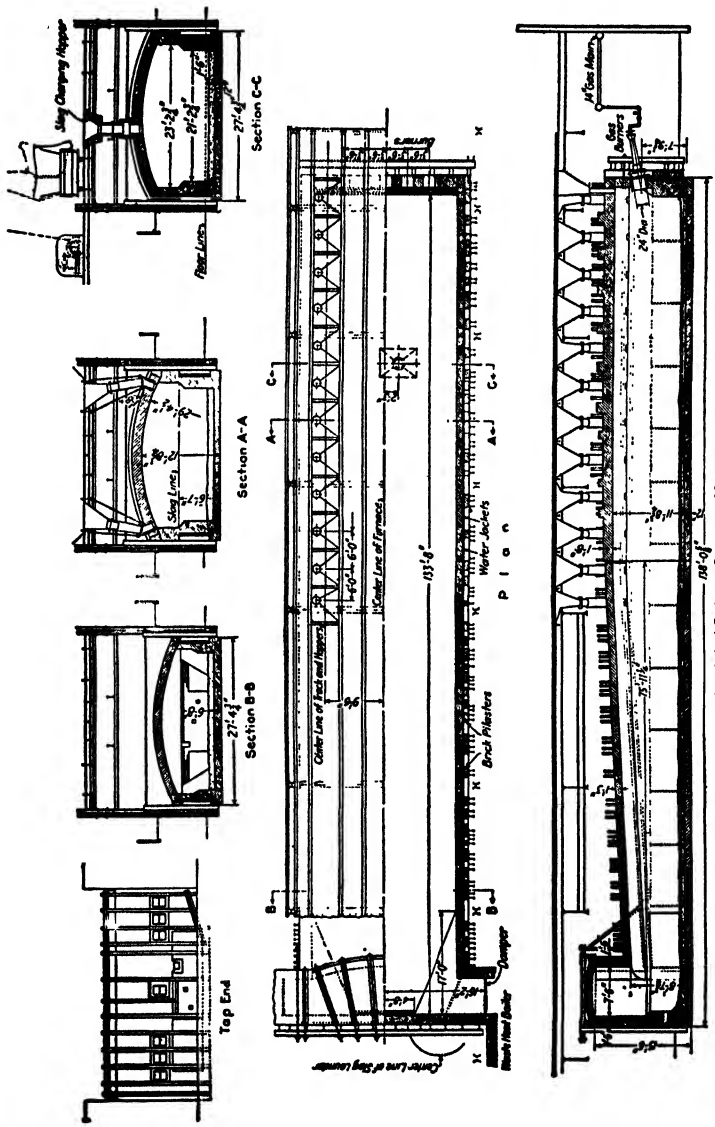


FIG. 342. Reverberatory copper-matting furnace. (*Courtesy of American Institute of Mining and Metallurgical Engineers, Paper by Frederick Laist.*)

these furnaces is beginning to be recognized as good practice, and probably all furnaces of this type will be insulated to some extent in the near future.

Copper Converters. Two types of converter are generally used at present known as the "Great Falls" (Fig. 343) and the "Peirce-Smith"

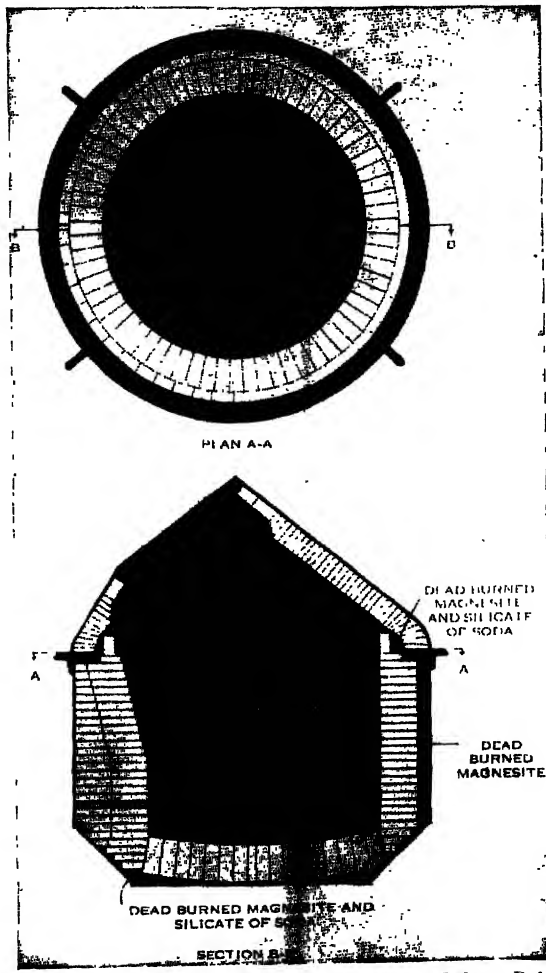


FIG. 343. Copper converter, Great Falls type. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

(Fig. 344). In the Great Falls type, the horizontal section is circular; whereas in the Peirce-Smith type, it is rectangular. The converters are mounted on trunnions for pouring the slag and metal, and the capacity runs from 100 to 300 tons per day. Converters are almost always lined

with magnesite brick backed up with some magnesite grain between the lining and shell. Some unburned magnesite brick have been tried in converters, apparently with considerable success. The life of these linings is quite long, averaging 5 to 10 years, as a layer of magnesite is built up on

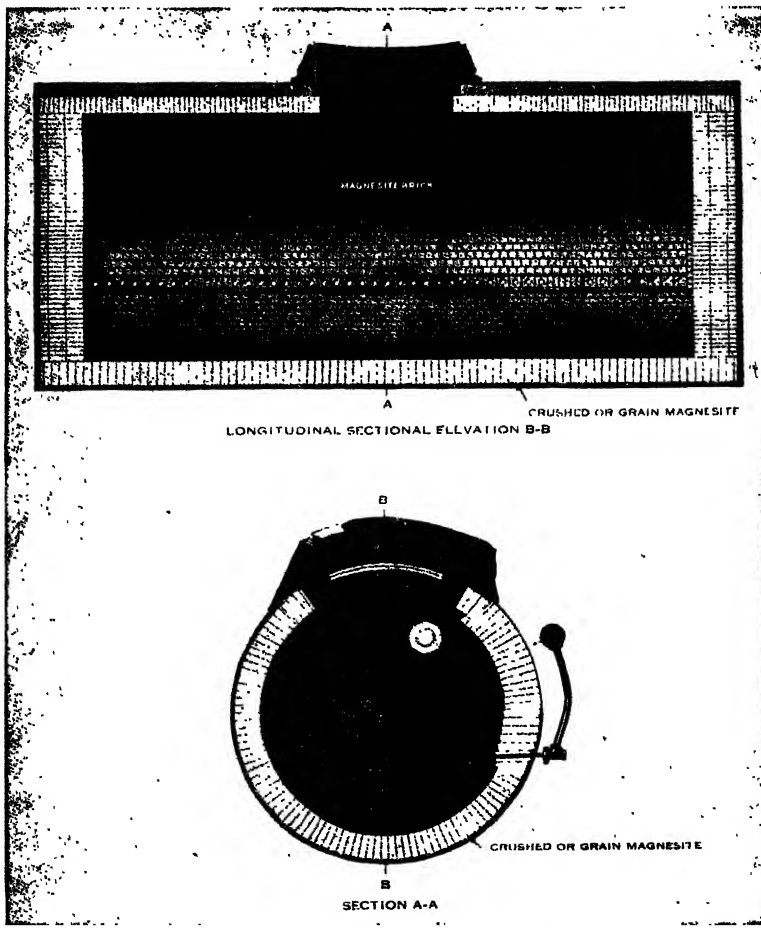


FIG. 344. Copper converter, Peirce-Smith type. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

the inner surface and protects the lining. Around the tuyères, however, the cutting action may be quite severe, and repairs have to be made in this zone after about 6 months or less.

Copper Anode Refining Furnace. Most of these furnaces are of the reverberatory type, perhaps 35 ft long and 15 ft wide, with a capacity of

250 to 400 tons of copper. The fuel is oil, pulverized coal, or gas, firing being from one end. After melting, air is blown into the bath to saturate with Cu_2O, while a small amount of siliceous flux is sometimes added to slag the base metals. The slag is then skimmed off; the charge covered with coke and poled to reduce the Cu_2O. The refining cycle takes somewhere around 24 hr. The bottoms of these furnaces are quite similar to the bottoms of the smelting furnaces, *i.e.*, ganister rammed on top of clay brick. In the melting operation, at the surface of the ganister is formed copper silicate, which acts as a cementing material to give a strong, firm body. Often bottoms are kept cool by air circulating through pipes running under the bottom. Though requiring occasional patching, bottoms may last from 3 to 5 years. In the side walls, magnesite brick are used to slightly above the slag line, beyond which silica brick are generally used. Above the slag line, chemically bonded and metal-cased magnesite brick have been successfully tried, giving a life of 200 heats.

The roof of the refining furnace is generally of silica brick, but it is actively attacked by the copper oxide slag thrown against it during the poling operation. Thus the roof has a life of only 100 to 125 heats. Magnesite and forsterite bricks have been tried in the roofs to some extent, with somewhat increased life.

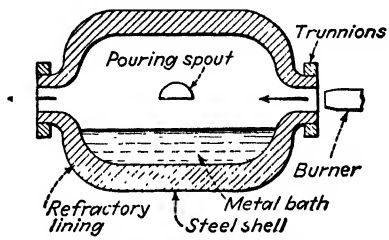


FIG. 345. Open-flame brass-melting furnace.

Wire-bar Furnaces. The operations producing wire bars and other commercial shapes from copper cathodes are practically the same as those for producing anodes. The furnaces are very similar to the anode furnaces previously discussed, except the bottom is made of silica brick instead of silica sand. Side walls are made of magnesite to slightly above the slag line, and either silica or magnesite brick are used up to the arch. In the upper parts of the side wall, both unburned and metal-case brick have been successfully tried. The roofs are usually made of silica, although magnesite brick have been used with a somewhat greater life.

2. Melting Copper Alloys. *Types of Furnace.* The melting of brass and other copper alloys is carried out in gas- or oil-fired furnaces with a shallow hearth and an open flame; but for smaller lots or high-zinc alloys, plumbago crucibles are used. The indirect-arc furnace in a rotating cylindrical shell is much used, but recently, however, the induction-type melting furnace of the Ajax-Wyatt type is favored.

Open-flame Melting Furnaces. In Fig. 345 is shown a tilting furnace of this type in which the oil burner is introduced through one end and the

TABLE 115. CLASSIFICATION OF REFRACTORIES FOR THE COPPER INDUSTRY

(Adapted from Industrial Survey of the Conditions Surrounding Refractory Service in the Copper Industry, "Manual of ASTM Standards on Refractory Materials")

	Furnace part	Material	Temperature	Load	Spalling	Slagging action	Abrasion	Life	Remarks
Roasting Process									
Roasting furnace	Lining	High-heat-duty fireclay brick; insulating brick between lining and shell	1500°F. (815°C.), max.	Moderate	Slight	None	Important		
	Hearths	High-heat-duty fireclay brick	1500°F. (815°C.), max.	Moderate arch stresses	Slight	None	Important		
Smelting Process									
Smelting furnace, reverberatory	Side walls	Silica brick, magnesite brick	Approximately 2800°F. (1540°C.)	15 lb. per sq. in., max.	Slight	Severe	Moderate		
	Bottom	Silica sand, silica brick, magnesite brick, chrome brick; silica sand largely used	2500 to 2800°F. (1370 to 1540°C.)	Unimportant	Unimportant	Severe	Moderate		
	Roof	Silica brick, magnesite brick, suspended unburned magnesite brick, forsterite brick (in certain portions)	2800°F. (1540°C.), max.	Arch stresses in sprung construction	Usually slight, although may be cause for premature failure	Important	Moderate	100 days	
	Firewall	Fireclay brick, silica brick, magnesite brick	2850°F. (1565°C.)	10 lb. per sq. in., max.	Moderate	Important	Moderate		Conditions for direct coal fired. Where gas, oil, or powdered coal is used, combustion takes place in furnace proper
	Front wall	Silica brick, magnesite brick, fireclay brick, high-alumina brick	2400°F. (1315°C.), max.	10 to 15 lb. sq. in.	Slight	Severe	Moderate		
	Waste heat boilers	Fireclay brick, silica brick	2300°F. (1260°C.), max.	15 to 20 lb per sq. in.	Slight	Important	Moderate		Waste heat boilers commonly used

	Furnace part	Material	Temperature	Load	Spalling	Slagging action	Abrasion	Life	Remarks
Converting Process									
Converter	Lining	Magnesite brick	2400°F. (1315°C.)	Unimportant	Temperature drops to 1200°F. during charging. Spalling unimportant for bottom half of lining; moderate for upper half	Moderate on basic lining	Erosion severe	5–10 years	
Refining Process									
Refining furnace	Furnace roof	Silica brick	2800°F. (1540°C.), max.	High	Moderate to severe	Severe	Slight	100–125 heats	
	Furnace bottom	Silica brick, magnesite brick	2300°F. (1260°C.), max.	High	Slight	Severe on silica brick at junction of bottom and side wall	Severe	3–5 years	
	Furnace side walls	Front walls and from bottom to just above metal line in back wall, magnesite brick	2700 to 2800°F. (1480 to 1540°C.)	Moderate	Severe in front wall piers or jambs	Severe	High at charging doors		
		Back walls above metal line: magnesite brick, silica brick, fireclay brick		Moderate	Severe on magnesite brick	Severe on silica or fireclay brick	Slight		
	Combustion chamber	High-heat-duty fireclay brick	2800°F. (1540°C.), max.	Moderate	Moderate to severe	Varies with fuel	Varies with fuel		
	Uptakes	Magnesite brick, high-alumina brick, silica brick, high-heat-duty fireclay brick	2800°F. (1540°C.), max.	Moderate	Moderate	Severe at intake	Moderate		
	Waste heat boilers	High-heat-duty fireclay brick	2700 to 2800°F. (1480 to 1540°C.)	Moderate	Moderate	Moderate	Slight		
Holding furnace	Bottom and side walls	Usually magnesite brick	Approximately 2300 to 2400°F. (1260 to 1315°C.)	Roof high; remainder moderate	Moderate to severe	Moderate to severe	Slight		
	Roof	Silica brick, magnesite brick, forsterite brick							

charge is put through a door in the side of the shell. The shell itself can be rotated on trunnions for pouring.

The linings of these furnaces are usually made from dense fireclay brick. For the hearth is used a rammed-in plastic material containing ganister, silicon carbide, or fused alumina with a clay bond. The refractories must

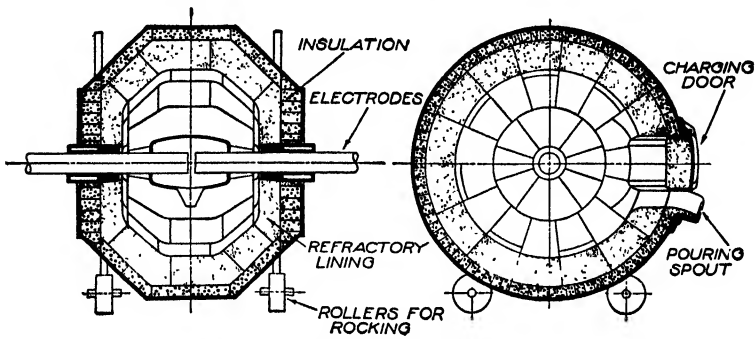


FIG. 346. Detroit rocking indirect-arc furnace. (*Redrawn from illustration by Huhlman Electric Company.*)

withstand spalling, and slag attack occurs occasionally. Five hundred to one thousand tons of brass can usually be melted in one lining.

Indirect-arc Melting Furnace. This furnace, as shown in Fig. 346, consists of a rotating, refractory-lining shell with an arc placed at the center of the axis so that the radiant heat falls directly on the metal bath and on the refractory walls. By rocking the furnaces, the hot refractory walls can be made to give up their heat to the metal bath and at the same time prevent the walls from being overheated. The lining is of high-alumina shapes or bricks, often with insulation. The furnace capacity runs from 250 to 2,000 lb, and as much as 1,000 tons of brass can be taken from a lining. Failures usually occur as a result of metal penetration in the lining and disintegration due to zinc dust.

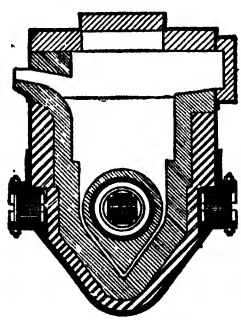


FIG. 347. Section of Ajax-Wyatt furnace. (*J. Am. Ceram. Soc.*)

The Induction Melting Furnace. This type of furnace, as shown in Fig. 347, consists of a crucible for holding the metal, and extending from the bottom of it is a U-shaped channel, which forms a one-turn secondary of a transformer by passing around its core. By means of the induced currents, the molten metal circulates through this U-shaped channel and heats the charge in the crucible. Of course, furnaces of this type must be started by a small amount of melted metal, after which pigs can be added.

From the refractory point of view, the greatest difficulty with these furnaces is the U-shaped passage or slot, which has a cross section of only a few square inches and must have thin walls to give a high efficiency. If any cracking occurs and molten metal runs down on to the transformer coil, the furnace is, of course, put out of commission and has to be rebuilt. It ceases to operate after a time because of gradual plugging of the slot by sludge. The refractory that has been found quite successful for these furnaces melting yellow brass is a plastic mixture of asbestos and fireclay, Adams[19] reporting an 8-year life in one case. Booth[26] reports 12 million pound heats in a fused-alumina rammed lining for yellow brass. For higher temperature alloys, electrically fused magnesite and silicate of soda, carefully rammed into the furnace shell, have been used. Fused alumina with clay and magnesia-alumina ramming mixtures have also been used. In some cases, prefired shapes of flint clay have proved successful. A life of 600 heats for copper and 50 to 250 heats for nickel and its alloys has been reported.[18,20]

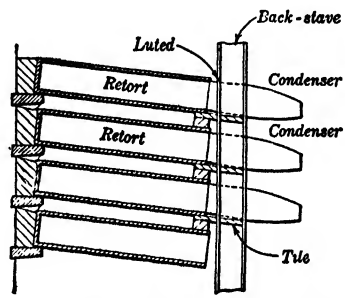


FIG. 348. Details of zinc retorts and condensers. (*From J. L. Bray, "The Principles of Metallurgy."*)

3. Zinc. *Outline of the Process.* Zinc ores, which usually contain sulfides but occasionally consist of carbonates or silicates, are generally concentrated by ore-dressing methods to produce a concentrate high in zinc. This concentrate is then desulfurized by roasting or sintering and reduced by carbon at a temperature of 1100 to 1300°C (about 2010 to 2370°F). Because of the fact, however, that metallic zinc is volatile below the temperature at which ZnO is reduced, the process must be carried out in closed vessels with enough excess carbon to prevent oxidation of the vapor. The zinc vapor coming from these closed vessels or retorts is condensed in the liquid form at temperatures around 425 to 500°C (about 800 to 930°F).

Most of the zinc is made in comparatively small retorts of only 2 or 3 cu ft capacity by the batch process. Recently, however, continuous smelters have been in operation.

Batch Zinc Distilling Furnaces. The zinc retort, a cross section of which is shown in Fig. 348, is about 8 to 9 in. in inside diameter and 4 to 5 ft long. At the open end is attached the condenser, which tapers down to a diameter of about 3 in. for the escape of the gas. Both the condenser and retort are made of fireclay mixtures, a Missouri fireclay generally being preferred in this country because of its good hot strength. Although the retorts used to be handmade, they are made, at present,

entirely by machine, such as a hydraulic press. A good density of structure is necessary to prevent loss of zinc vapor through the walls and also to prevent too much zinc from being lost in the pores of the retort when it is rejected at the end of the run. Some plants find that retorts containing 75 to 85 per cent silicon carbide give enough greater life to pay for this more expensive material.

These retorts with their condensers are set up in banks of 200 or 300 in a long gas-fired furnace, as shown in Fig. 349, usually of the Belgian

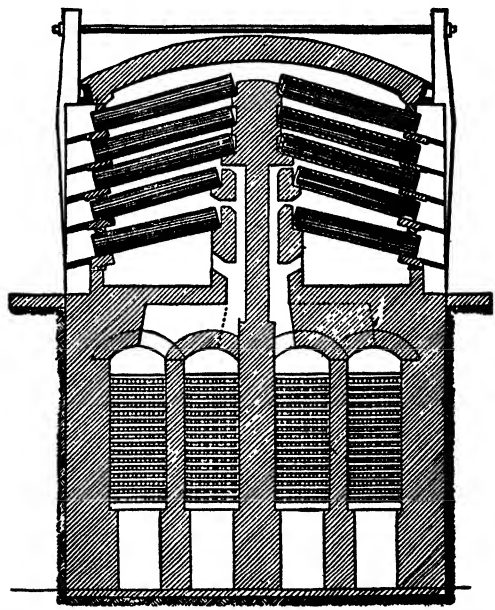


FIG. 349. A cross section of a Belgian zinc distillation furnace. (*From "An Outline of Metallurgical Practice," by C. R. Hayward, courtesy of D. Van Nostrand Company, Inc.*)

type. A center wall running down the middle of the furnace holds the back end of the retorts, whereas the front end is luted into the wall of the furnace. The firing is usually regenerative, and temperatures of 1250 to 1350°C (about 2280 to 2460°F) are reached inside the retorts, whereas outside temperatures as high as 1450°C (about 2640°F) are sometimes employed. This necessitates a rigid retort to carry the load at these temperatures, and it also means that the center wall of the furnace must be of a high-quality refractory. The side walls of the furnace are usually made of fireclay brick, whereas silica brick would be used for the center wall and roof. Hard-fired, high-alumina brick have been tried in the center walls and should give good results. The life of the retort runs from 30 to 40 days, but the furnace itself, being quite free from slagging

TABLE 116. ANALYSIS OF REFRACTORY SERVICE IN THE ZINC INDUSTRY

Furnace part	Material	Temperature, °F.	Load	Spalling	Slagging	Abrasion	Life	Remarks
Retorts	Flint fireclay. Dense structure	2280–2460	Important	Slight	Some	Slight	30–40 days	Silicon carbide retorts have been tried
Condensers	Flint fireclay. Dense structure	Low	Low	Slight	None	None		
Smelting furnace side walls	High-heat-duty-fireclay brick	2500–2640	Unimportant	Unimportant	None	None	2–3 years	
Smelting furnace center wall	Silica or super-duty fireclay brick	2500–2640	Important	Unimportant	None	None	2–3 years	50 per cent alumina brick have been tried here
Smelting furnace roof	Silica	2500–2640	Arch stresses	Unimportant	None	None	2–3 years	

action, gives a life of several years without repairs. Table 116 gives the service conditions for this type of furnace.

The Continuous Zinc Distilled Furnaces. The continuous furnaces, as developed by the New Jersey Zinc Company, use a vertical retort constructed of silicon carbide with a section of about 1 by 5 ft and a height of 20 to 25 ft. The briquetted charge of coal and zinc ore is continuously fed in the top, and the distilled zinc is collected in condensers around the top of the shaft while residues are discharged at the bottom. A single retort has a capacity of about 6 tons of zinc per day, and the life of the continuous retorts is estimated at 3 years. The furnaces in which these retorts are placed are fired with gas.

The Electrothermic Zinc Furnace. This type of furnace has been described by MacBride.[33] It is a vertical shaft heated by electrical resistance of the charge itself. The refractories composing the shaft must have a low porosity to prevent zinc penetration, high softening point, and high electrical resistance.

4. Lead. *Outline of the Process.* Lead ores are usually sulfides, of which the mineral galena is most common. The ore is concentrated by selective flotation, and the lead concentrate is sintered to a firm mass, usually in the Dwight Lloyd type of continuous machine, which does not employ any refractory. In this process, most of the sulfur is driven off as SO_2 and the lead is converted to an oxide. The process also produces the ore in a lump form, which is more suitable for the smelting operation. The smelting generally takes place in a water-jacketed blast furnace in order to slag off the impurities contained in the ore and to reduce the lead oxide to molten lead. The larger part of the molten lead is removed from the furnace through a "siphon tap," which passes through the crucible wall to the bottom of the crucible. The slag with some occluded lead is tapped from the furnace and allowed to separate in a settler from which the slag overflows to a slag car. The lead is tapped out periodically.

The Lead Blast Furnace. The lead blast furnace, as shown in Fig. 350, indicates that very little is used in the way of refractories because of the almost complete water jacket. However, there are refractories, usually high-duty fireclay brick of good density, in the upper part above the water jacket. Abrasion is the most important factor here, as the temperature is comparatively low. Refractories are also used in a crucible below the tuyères, but here again the temperature is not very high, and therefore the refractory requirements are chiefly low porosity and hardness and resistance to the action of molten lead. Dense firebrick are used in the crucible, but it is important that the joints between them be very thin, and often a chrome-base mortar is used for a jointing material. In some cases, plastic refractories of fireclay grog, ash, and coke are rammed into the

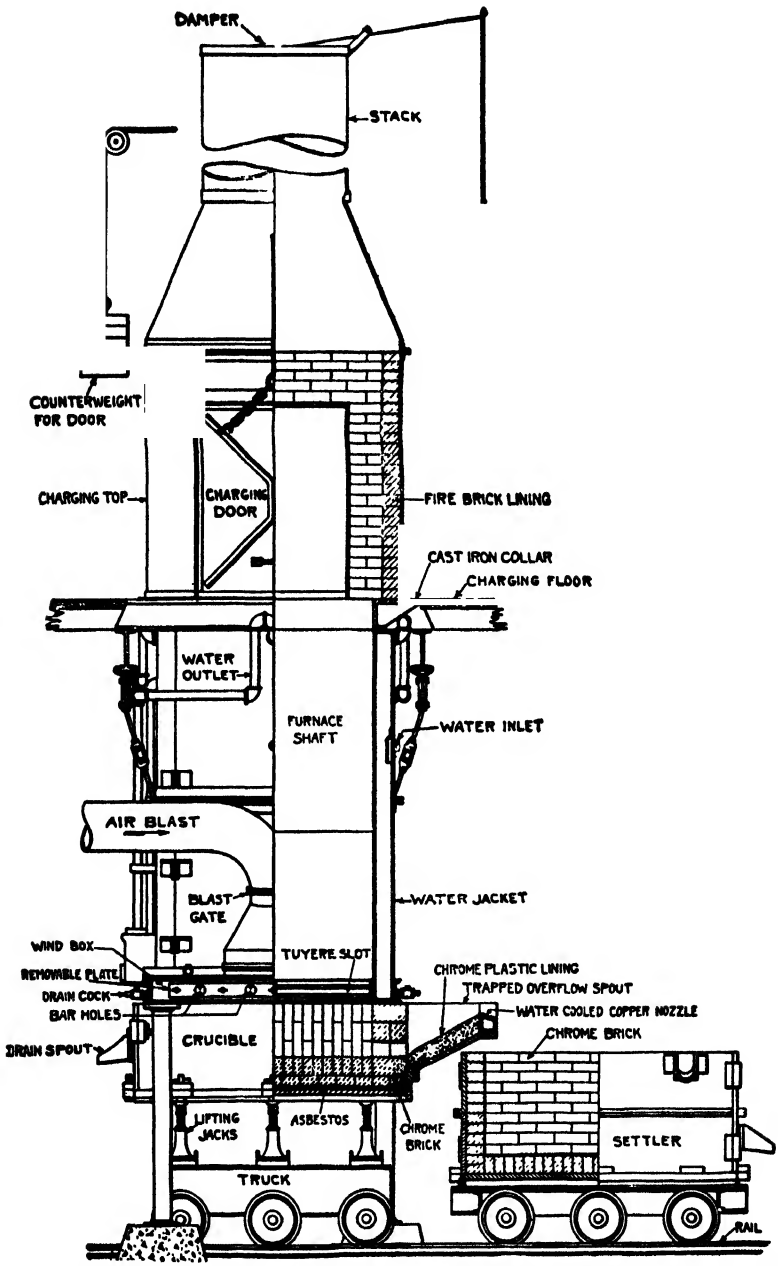


FIG. 350. Sectional view of lead-smelting furnace, matting type with outside settling. (*Courtesy of Mr. C. H. Mace, The Mace Company, Denver, Colorado.*)

crucible. Chrome plastics are also used to some extent, especially for the overflow spout.

Lead-refining Furnaces. Molten lead that comes directly from the blast furnace or from the desilvering kettles is treated in a reverberatory type of refining furnace somewhat as shown in Fig. 351. Air is blown into the bath to oxidize iron, arsenic, antimony, and tin to dross, and the latter is

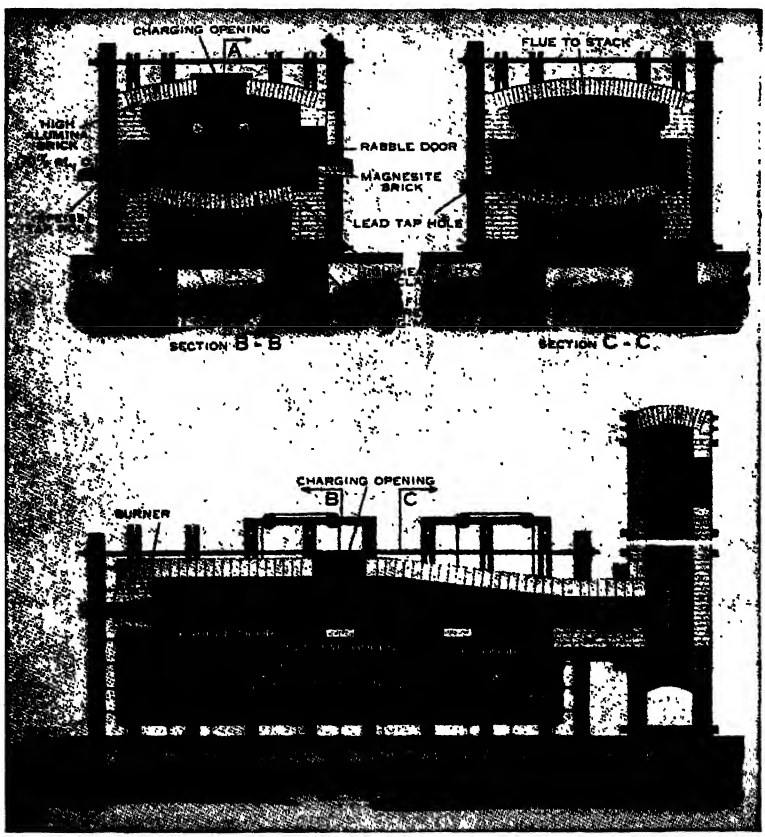


FIG. 351. Typical lead-drossing furnace. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

skimmed off and retreated. High refractoriness is not required, as the maximum temperature is around 1100°C (about 2000°F). Temperature changes are not particularly great; consequently, spalling is not a problem. Slag action is the most serious trouble, as the action of lead oxide is very severe in contact with most types of refractories. Magnesite brick are now generally used in the side walls to somewhat above the slag line, but

TABLE 117. CLASSIFICATION OF REFRACTORIES FOR THE LEAD INDUSTRY
(Adapted from Industrial Survey of Conditions Surrounding Refractory Service in the Lead Industry, "Manual of ASTM Standards on Refractory Materials")

Class	Furnace part	Material	Temperature	Load	Spalling	Slagging action	Abrasion	Remarks
Blast furnace	Lining	High-heat-duty fireclay brick, chrome cement	2200°F. (1205°C.)	15 to 20 lb. per sq. in.	None	Not severe	Important	Bottom part of furnace where highest temperature prevails is made of water-cooled cast iron. Density is main requirement of refractories
Refining furnace	Bottom	High-heat-duty and intermediate-heat-duty fireclay brick	2000°F. (1095°C.)	Unimportant	None	Important	Moderate	
	Side walls and end walls above metal line	High-heat-duty and intermediate-heat-duty fireclay brick	2000°F. (1095°C.)	10 lb. per sq. in., max.	Temperature change during charging, spalling slight	Important	Moderate	
	Side walls and end walls at and below metal line	Fireclay brick, magnesite brick, high-alumina brick	2000°F. (1095°C.)	10 lb. per sq. in., max.	Very slight	Very important	Moderate	
	Roof	High-heat-duty and intermediate-heat-duty fireclay brick	2000°F. (1095°C.)	Arch stresses only	Moderate	Important	Very slight	
	Refining fire furnace box	Fireclay brick, largely high-heat-duty brick	2000°F. (1095°C.)	10 to 15 lb. per sq. in.	Moderate	Moderate	Moderate	Conditions in firebox chamber vary depending upon whether oil, gas, or coal is used as fuel
Drossing furnace	Bottom	High-heat-duty fireclay brick		Unimportant	None	Important	None	
	Side walls	Magnesite brick or high-alumina brick		Unimportant	Slight	Severe	None	
	Roof	Magnesite brick or high-alumina brick		Unimportant	Moderate	Moderate	None	

high-alumina brick have also been tried. The upper parts of the furnace may consist of a medium-duty firebrick with moderate resistance to spalling. The life of a brick in the upper wall depends a great deal on the type of operation and the amount of antimony in the lead.

5. Tin. There are, at the present time, very few tin smelters in the United States; but in other countries, this is a comparatively important operation. Many types of smelting are used, depending on the kind of ore. The metallurgist is fortunate in having, as his raw material, tin oxide, which can be readily reduced to the metal without great difficulty. The older types of furnace constructed are small blast furnaces much like the ones used for copper and lead. More recently, however, reverberatory furnaces have been used similar to those for copper ores, though on a much smaller scale. As the temperatures are comparatively low and the tin oxide is not an extremely active flux, dense fireclay brick have been found adequate as refractories.

6. Aluminum. Aluminum is produced by the electrolysis of fused salts, a process that calls for no particular amount of refractories. Aluminum is melted, however, in the larger scale operations in small open-hearth furnaces holding about 20,000 lb of metal. The temperatures are comparatively low, and the aluminum oxide is not very active but builds up on the walls and must be regularly sliced off. A good grade of dense fireclay brick accurately sized and giving thin joints has proved quite satisfactory, although in some cases the molten aluminum has a tendency to attack the brick, perhaps causing a thermite reaction with the iron oxide particles as suggested by Burrows.[38] Recently zircon[40] refractories have proved excellent for this purpose.

7. Nickel. Nickel is smelted in much the same way as copper, the detailed process depending a great deal on the type of ore available. The melting of nickel is often carried out in small open-hearth furnaces that are made almost completely of a dense fireclay brick, although super-duty fireclay and 50 per cent alumina bricks have been used with considerable success in some of the later furnaces.

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General:

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CHAPTER XXIII

REFRACTORIES IN THE GENERATION OF STEAM POWER*

1. Development of Boiler Furnace Designs. The fuel used in early boilers was chiefly lump coal fired by hand or by stoker operating at a fairly low rate of heat input. In either case, solid firebrick walls formed an entirely satisfactory enclosure for the unit. In fact, the refractory gave very necessary aid to combustion by reradiating heat to the fuel-burning equipment. When oil and gas firing became popular, solid brick walls were also found to be satisfactory for these fuels at moderate furnace-heat inputs.

The introduction of pulverized coal firing greatly intensified the problem of slag attack of boiler furnace refractories. An accompanying and still continuing upward trend in the size of boiler unit (and consequently the height of wall) increased the structural load on the brickwork. An increase of furnace heat input, boiler rating, and steam temperature materially raised the furnace temperature to which the brickwork was subjected. These three factors made imperative the development of economical boiler furnace designs capable of withstanding far more severe conditions than can a solid firebrick setting.

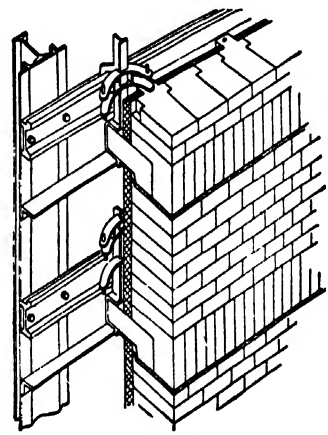

FIG. 352. Insulated, sectionally supported wall (American Arch).

Improvements in fuel-burning equipment, which paralleled the trends toward large, high-duty boiler units, now permit almost any type of fuel to be burned in a relatively low-temperature furnace. Therefore, most of the constructions that have evolved to take care of the previously described conditions of temperature, slagging, and load involve the use of partial or complete water cooling. For this reason, a large part of the present chapter deals with water-cooled furnace designs and the part played by refractories in supplementing them.

2. Modern Furnaces and Boiler Walls. The following types of wall constructions are often used on modern high-duty boiler units.

* This chapter was prepared by W. D. Stevens of the Babcock & Wilcox Company.

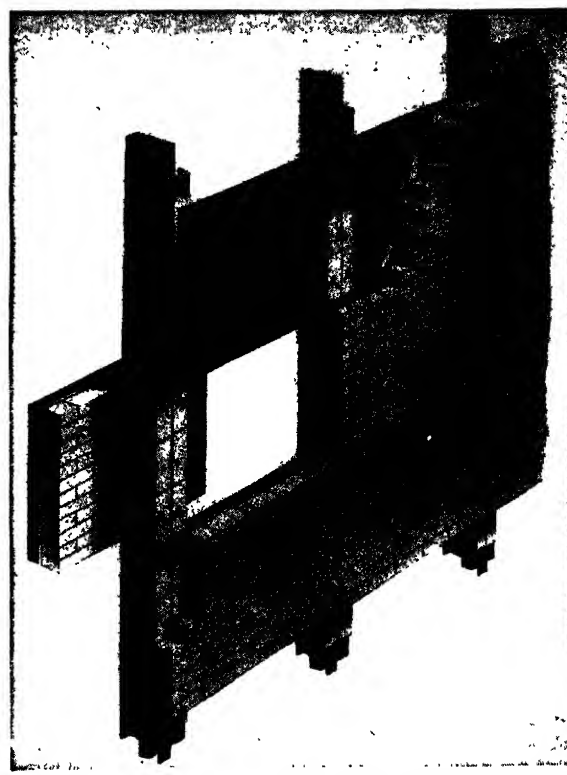

FIG. 353. Babcock and Wilcox insulating firebrick panel wall construction.

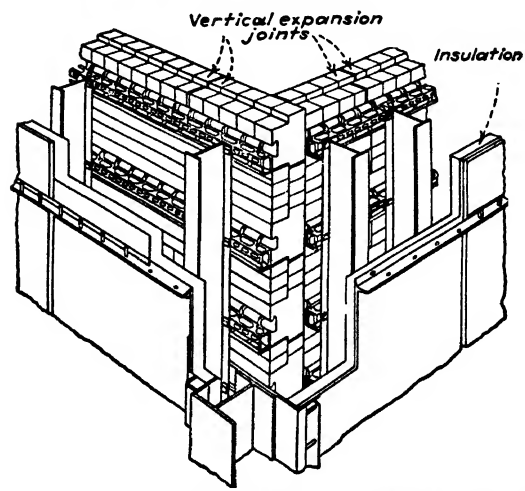

FIG. 354. Air-cooled, sectionally supported wall (Reintjes).

Sectionally supported walls divide the structural load and sectionalize the expansion of large walls by suspending the brickwork from castings that are, in turn, supported by external steelwork. There are many patented constructions of this type; among well-known ones are Detrick, Bigelow-Liptak, American Arch, and Reintjes.

Sectional walls may be made of tile only, of tile with insulation on the outside (see Fig. 352), or—in the absence of erosive conditions—of insulating firebrick (see Fig. 353). They are generally used for walls in the convection zone of the boiler or for low-duty furnace walls but can be

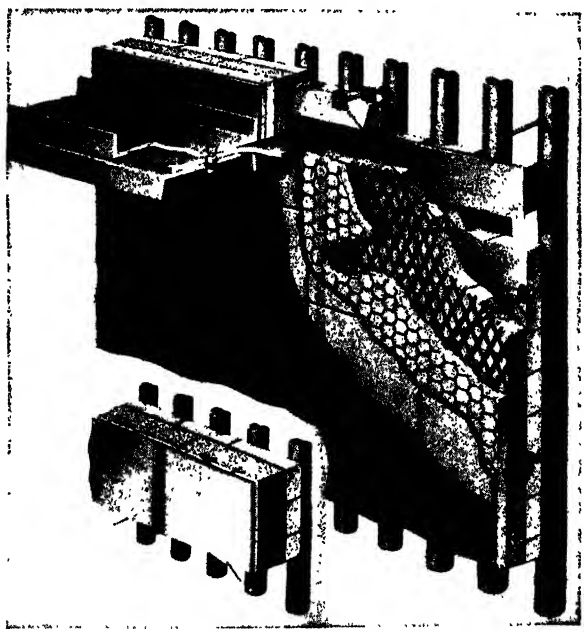

FIG. 355. Tube and brick wall. (*Babcock & Wilcox Company.*)

adapted to moderate-duty furnaces by facing with high-temperature brick or by air cooling (see Fig. 354). They have also been used for high-duty oil- , gas- or stoker-fired furnaces as a backing for waterwall tubes but in this application are more expensive than other types of water-cooled walls.

Tube and refractory walls (Fig. 355) are made up of waterwall tubes, which are part of the heat-absorbing surface of the boiler, spaced at intervals and backed with 2 to 3 in. of firebrick or tile. The brickwork is sufficiently cooled by the tubes to allow this type of wall to be used on the boiler convection zone for any type of firing, on high-duty furnaces fired by gas or stoker, and on low-duty pulverized-coal-fired furnaces. The

limiting factor with pulverized-coal furnaces is excessive slag accumulation rather than deterioration of the refractory.

Although temperature conditions do not dictate it, the refractory behind the tubes is usually of the high-duty type in order to obtain good slagging and fly ash erosion resistance and to take advantage of the closer sizing and warpage tolerances that may be expected from first-quality material. To prevent air leakage into the setting and to give structural strength, the brick or tile are normally laid in an air-setting mortar. In zones of high draft, further sealing can be accomplished by a backing of castable refractory reinforced by expanded metal lath. To give a reason-

FIG. 356. Outside view of tube and brick waterwall with insulation removed. (*Babcock & Wilcox Company.*)

able external surface temperature, the refractory is insulated with block insulation or insulating firebrick. For protection and appearance the external surface of the insulation is covered by a metal casing or a finish coat of plastic insulation.

The refractory and insulation are held in place by steel or alloy studs, which tend to sectionalize the structural loading of the walls. The wall tube spacing may be proportioned to give an operating refractory temperature about twice that of the boiler-pressure part temperature. Since the coefficient of expansion of firebrick is about half that of steel, this arrangement permits the refractory envelope to be continuous around the boiler setting without the provision of expansion joints. With expansion joints eliminated, the boiler setting will remain tight with a minimum

amount of maintenance. A tube and brick wall built without expansion joints is shown stripped of all insulation in Fig. 356. At the time of this photograph, the boiler had been in service for 7 months and during this period had undergone a heating and cooling cycle once each 24 hr.

Closely spaced tube walls (see Fig. 357) made of touching waterwall tubes can be used for any type of firing to form a continuous steel envelope

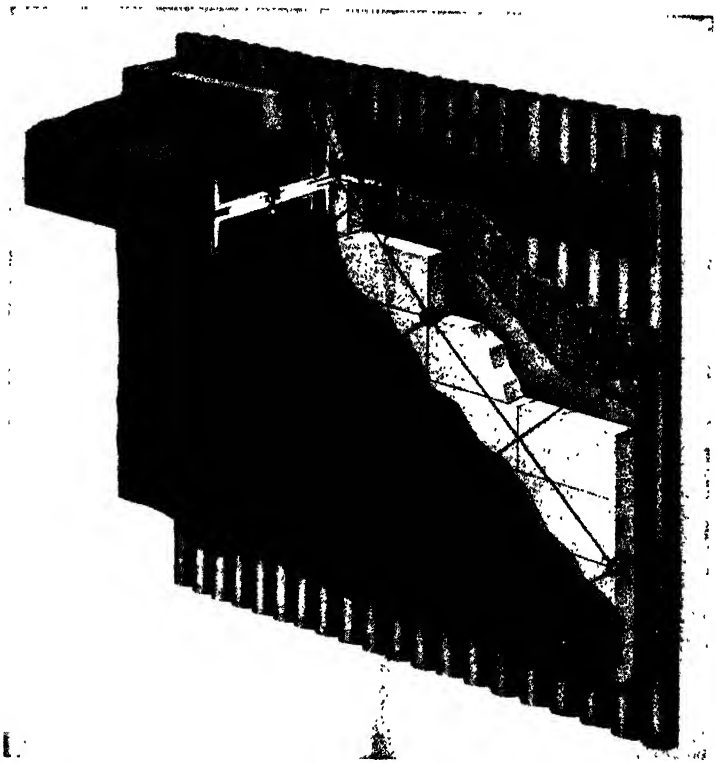

FIG. 357. Closely spaced tube waterwall. (*Babcock & Wilcox Company.*)

enclosing the furnace of a steam-generating unit. When its area is properly proportioned, such an enclosure will eliminate trouble from excessive accumulation of slag. It is usually sealed against air leakage with insulating concrete, insulated with block insulation or insulating firebrick, and covered with a metal casing or a plastic insulation finish.

The castable refractory backing is reinforced with expanded metal lath placed close to its outer surface, which makes the castable act as a reinforced concrete mat outside the tubes. Application of the concrete may be by hand or by cement gun. In either case, the metal lath is

installed on the wall first and the castable applied through it, so that the lath will act as a form.

This construction, like the tube and brick wall, can be made with no expansion joints. The drying shrinkage of the castable (about 0.5 per cent at 600°F) plus a small difference between the thermal expansion of the boiler steel and the castable (the castable coefficient of expansion is about two-thirds that of steel) results in a small theoretical difference between the width and height of the tube wall and that of the refractory

FIG. 358. Outside view of closely spaced tube waterwall showing castable refractory after use. (*Babcock & Wilcox Company.*)

backing after the unit has been brought up to operating pressure. The effect of this slight differential expansion is a series of hairline cracks very well distributed by the reinforcing metal lath. The resultant enclosure is tighter against air leakage than one with expansion joints and requires very little maintenance. Figure 358 shows the back of a closely spaced furnace tube wall after 12 months' service with a complete cooling and heating cycle once each week.

Flat stud tube walls are intended for use under similar conditions to those for which the closely spaced tube walls are used. They are somewhat more economical in their use of steel, since they are composed of tubes spaced at intervals. Each tube has a series of flat, rectangular steel plates welded along its entire length on both sides. The plates or studs on

two adjacent tubes close the space between them and present a practically continuous metal surface to the furnace. This type of wall is backed by the arrangement of castable refractory, insulation, and casing or plastic insulation finish previously described for closely spaced tube walls.

Partial or full stud walls are used where a higher furnace temperature than that obtainable from closely spaced tube or flat stud tube walls is desired. They are made up of waterwall tubes spaced at intervals. The space between the partial stud tubes is partially closed with two rows of round studs or rods welded to each side of the entire length of each tube. On the full stud walls, the entire furnace side of the tubes is covered with studs. The studs are packed with a chrome-base plastic pounded in place or a chrome-base castable gunnited or troweled in place to form a continuous wall. When in service, the chrome refractory is, in effect, water cooled because of the extended heat-transfer surface effect of the studs. The stud tube walls are sealed against air leakage and insulated in a manner similar to that used for closely spaced and flat stud walls.

One particular application of stud tube walls is the slag-tap furnace, where it is necessary to keep the coal ash above its fluid temperature in order to remove it as a liquid. This construction is very resistant to the fluid slag found in this type of furnace.

3. Slag-tap Furnace Floors. The floor of a furnace designed for liquid removal of coal ash must hold a pool of liquid slag that usually contains a high percentage of iron oxide. Therefore, it is a difficult refractory problem. This condition has been taken care of by making the floor of cast-iron Bailey blocks clamped tightly to tubes that are part of the boiler steam-generating surface as are the waterwall tubes. The blocks are covered with several inches of tightly packed chrome plastic or castable.

4. Boiler Baffles. Present-day refractory boiler baffles must be gastight enough to prevent leakage against high draft differentials. Although the cooling effect of the boiler tubes makes their service temperatures fairly low, the baffles are often made of high-duty firebrick or tile to assure high strength and erosion resistance. Gastightness is obtained by laying the brick or tile in an air-setting mortar.

Refractory baffles may also be made of a dense castable reinforced where necessary by alloy or steel rods.

5. Boiler Unit for Multi-fuel Firing. Figure 359 shows a steam-generating unit arranged for firing pulverized coal, oil, or gas either singly or in combination. The various wall constructions and refractory parts are labeled on the illustration.

The furnace cooling surface is proportioned to keep the temperature of the gases leaving the furnace below the ash initial deformation temperature (oxidizing basis) when pulverized coal is fired. This keeps most of the coal

ash in the furnace in a dry state and permits it to slide down the sloping hopper to the ashpit (not shown), which may be flooded with water or may be dry with a water sluice system. The ashpit lining is subjected to thermal shock due to the impingement of the water on the hot refractory. It may be of a castable refractory or of a high-duty firebrick selected for good spalling resistance.

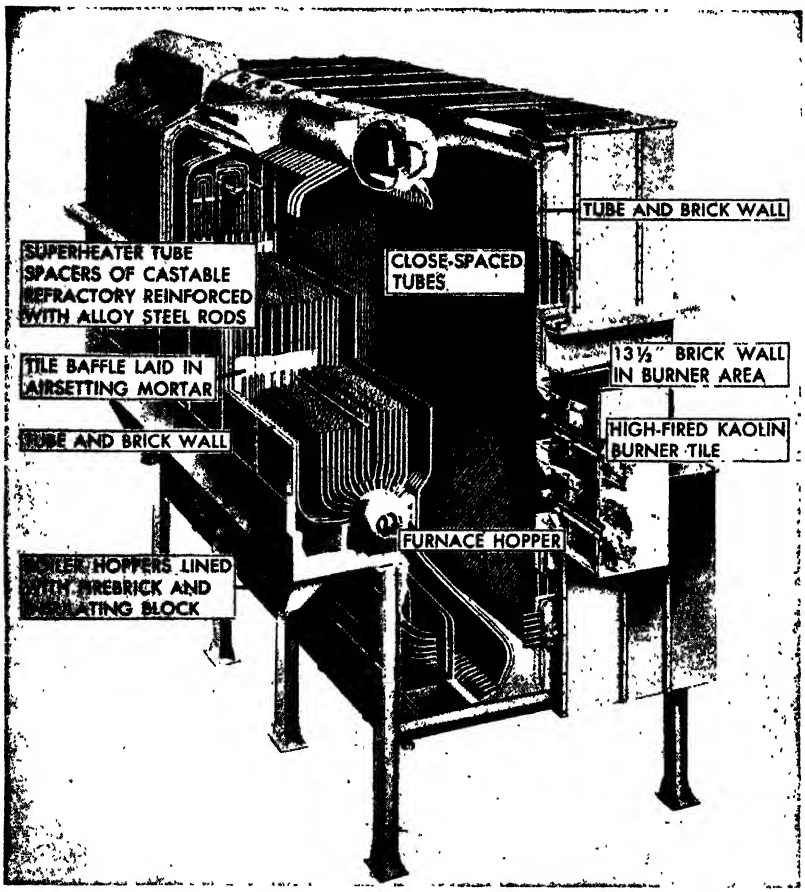

FIG. 359. Babcock and Wilcox integral furnace boiler with hopper-bottom furnace.

6. Pulverized Coal-fired Boiler (Slag-tap Type). The unit in Fig. 360 is primarily designed for pulverized coal firing but is capable of full steam output while using oil fuel. In order to avoid the accumulation of ash deposits on the tubes of the boiler banks when coal is burned, the total furnace-cooling surface of this boiler is sufficient to make the gases leave the furnace at a temperature below the initial deformation temperature of

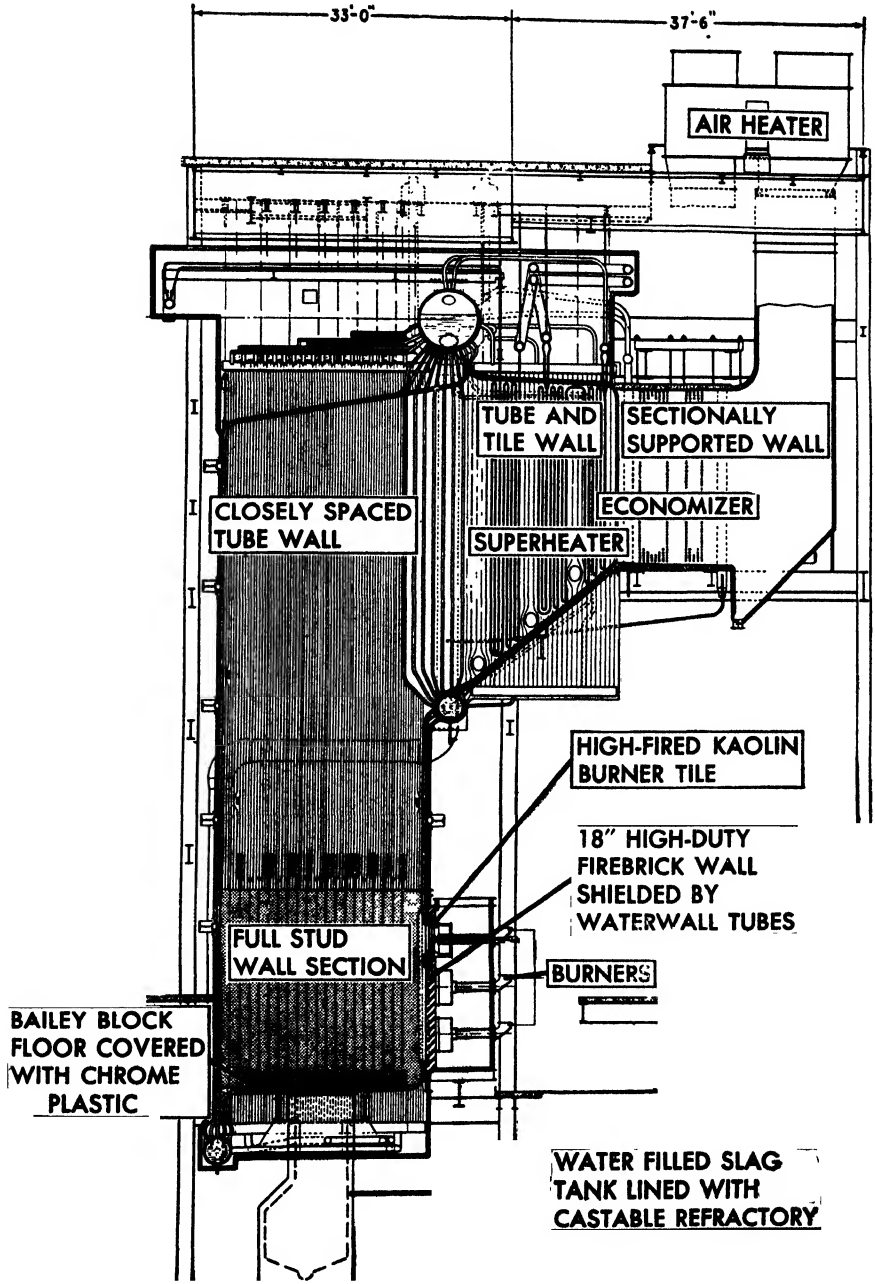

FIG. 360. Babcock and Wilcox radiant boiler with slag-tap furnace.

the coal ash. However, the location of burners and the use of fully studded tubes in the burner area make it possible to keep the temperature at the furnace floor high enough to melt the coal ash that collects there. The liquid slag thus formed drains continuously into a flooded slag tank. The

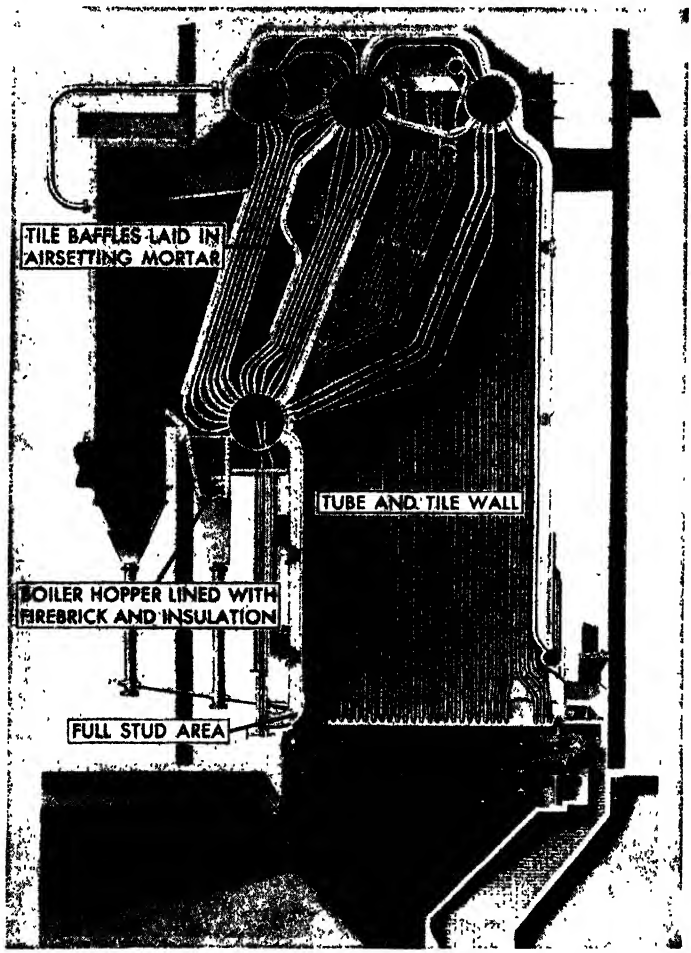

FIG. 361. Babcock and Wilcox sterling boiler fired by Detroil spreader stoker.

tank is lined with castable refractory, which must be highly resistant to spalling.

7. Cyclone Furnace. One interesting application of the full stud tube construction covered with chrome plastic or castable is the cyclone furnace, which burns crushed coal at a rate of heat input far exceeding that normally encountered with other types of firing. The cyclone is a cylinder about 8 ft

in diameter and 10 ft long constructed entirely of full stud tubes. Coal crushed to 0 to ¼ in. in an ordinary coal crusher is fed to one end of the cylinder, and the combustion air is admitted tangentially at high velocity. The coal burns rapidly while swirling around the cylinder walls in a film of fluid slag. The cyclonic action, in addition to promoting rapid combustion, permits a very high percentage of the ash to be removed from the furnace

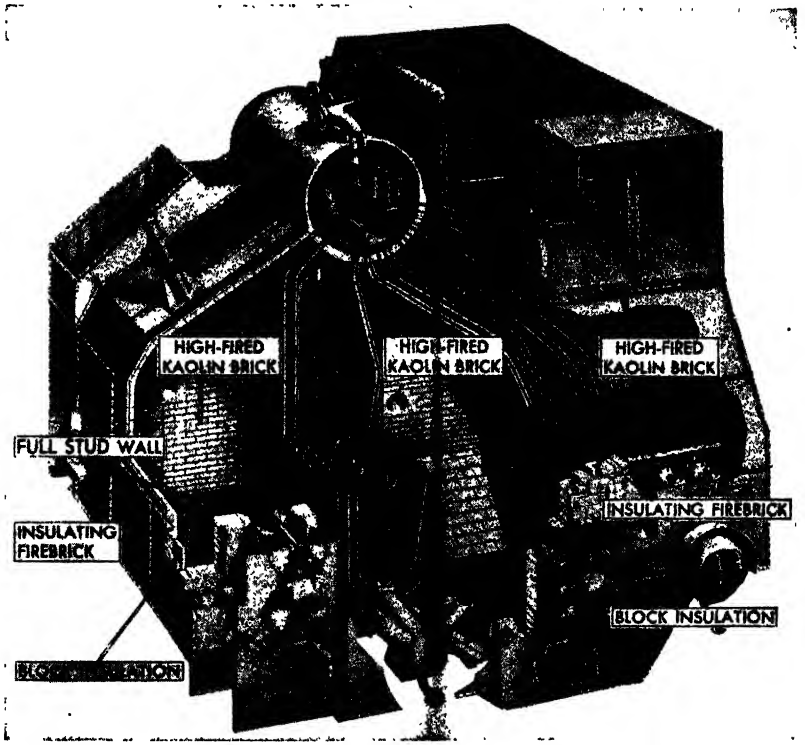

FIG. 362. Babcock and Wilcox single uptake controller super-heat boiler.

as slag. The products of combustion, which then enter a conventional water-cooled boiler furnace for further cooling, carry with them, entrained as fly ash, only about 10 per cent of the coal ash as compared with from 55 to 85 per cent for pulverized coal firing.

8. Spreader-stoker-fired Boiler. Figure 361 depicts a boiler fired by a spreader stoker. The bituminous coal is mechanically thrown into the grate from the front of the furnace. The grate moves slowly from rear to front and discharges the coal ash continuously.

The entire boiler and furnace enclosure is formed of tube and tile walls. The baffles are of tile laid in an air-setting mortar. On the rear wall just

above the stoker, the waterwall tubes are protected with full stud construction.

9. Oil-fired Marine Boiler. The marine boiler shown in Fig. 362 is a controlled superheat unit used to obtain high steam plant efficiency over a

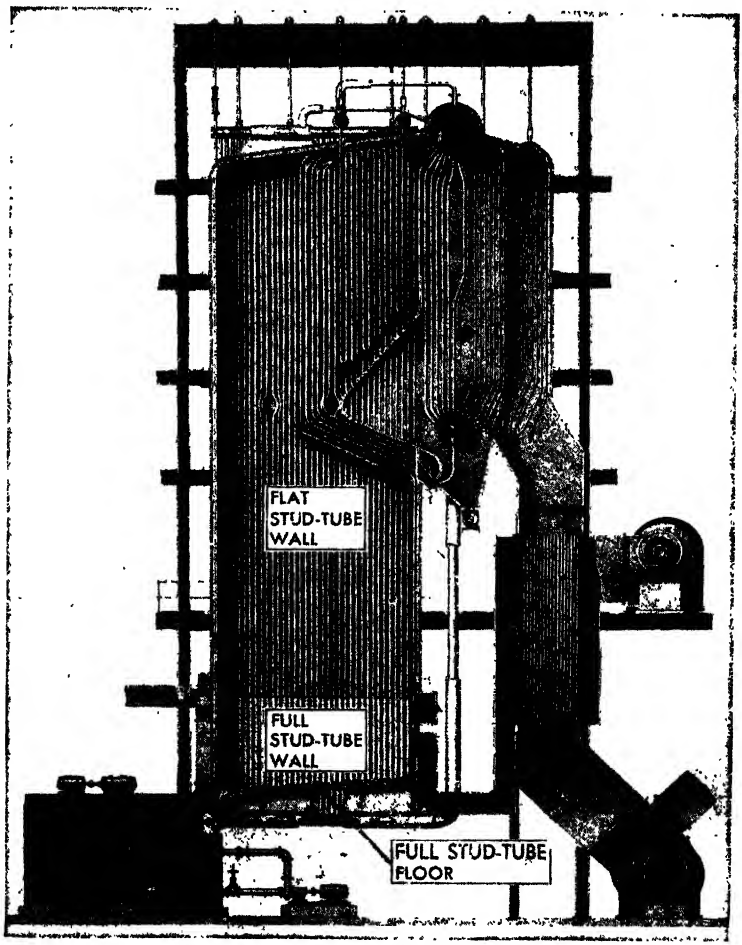

FIG. 363. Babcock and Wilcox two-drum recovery unit.

wide range of output. The furnace, which has an extremely high heat release, has one stud tube side wall. Owing to weight limitations, the front and rear walls are not water cooled. As shown, the uncooled refractory walls including the burner wall are built of high-fired kaolin brick held to the casing by anchor bolts and backed up by insulating firebrick and block insulation. However, on some of the more recent installations, the burner

wall has been made of a high-temperature kaolin-base castable refractory. The walls enclosing the boiler tube banks, where the temperature is too low for molten oil slag to exist, are made entirely of insulating firebrick to save weight.

10. Waste-heat Boilers. Waste-heat boilers are used in a great many industries for recovering heat in the flue gases from various types of industrial processes. Typical examples are the blast furnace and rotary cement kiln. The refractories used in the waste-heat boiler are always operated at comparatively low temperatures but, in general, are subjected to considerable abrasion, as most of the boilers operate under conditions where dust and ash are carried in the gases. For this reason, dense, high-duty firebrick are used for these conditions.

11. Black-liquor Recovery Furnaces. The economical operation of a modern pulp mill necessitates the recovery of chemical and heat values in the waste liquor. In the sulfate or kraft process, in which the recovery of chemicals is most generally employed, the wood chips are digested with a hot solution of sodium hydroxide, NaOH, and sodium sulfide, Na_2S, to remove the noncellulose portion of the wood. The spent cooking liquor (black liquor) is concentrated by evaporation until it contains from 55 to 65 per cent solids. It is then sprayed into a recovery furnace where it drops and falls to the floor as "char." On the floor, the carbonaceous material is burned with a deficiency of air. In the reducing atmosphere thus formed, the sodium salts are smelted out of the char. The resulting smelt containing mostly sodium carbonate, Na_2CO_3; sodium sulfide; a small percentage of sodium sulfate, Na_2SO_4; and traces of other sodium salts are discharged from a spout.

The conditions existing in this furnace are extremely severe as far as action on the refractories is concerned, primarily in view of the aggressive chemical activity of the fused sodium salts. In the earlier forms of recovery units, soapstone blocks were generally used as being the refractory best able to withstand the action of these molten sodium salts, but this material had a maximum life of only 10 to 12 months. In recent years, furnaces of this kind have been entirely water cooled with a high degree of success. Figure 363 shows a recovery unit having a water-cooled furnace. The upper walls are flat stud, while the lower walls and floor where a higher temperature is required are of full stud construction. The plastic chrome ore is quite resistant to the action of soda because it is inert chemically and is aided by the cooling action of the water tubes. This type of furnace requires little maintenance.

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CHAPTER XXIV

REFRACTORIES FOR USE IN NUCLEAR POWER PRODUCTION

1. Introduction. In order to discuss the possible future role refractory materials may play in the components of nuclear power plants, it will be necessary first to review the mechanism by which power is obtained from the atom. The history of the developments in nuclear physics, almost all written in the last ten years, is simply and clearly stated in the Smyth report[2] and therefore will not be discussed here.

2. The Nuclear Fission Process. *The Structure of the Atom.* The atom consists of a positively charged nucleus surrounded by negatively charged electrons. It is known that the chemical species is determined by the number of electrons about the nucleus and that this is represented in the case of neutral atoms by the atomic number. In chemistry we are concerned mainly with the electrons surrounding the atom, because it is these particles which enter into the various chemical reactions in forming compounds. Now it is necessary to go further and ascertain the structure of the nucleus itself, for this is the seat of nuclear power.

The atomic nucleus is now believed to be chiefly composed of a compact group of particles of two kinds; one the proton with a positive charge equal and opposite to the charge on the electron and the other the neutron with no charge at all. The number of particles in the nucleus is expressed by the mass number A. An element, therefore, can be written as ${}_{92}U^{238}$, where 238 is the mass number and 92 the atomic number, or number of protons Z. In a chemically neutral atom, the number of electrons equals the number of protons.

About 250 different nuclei exist in nature, ranging in charge and mass from ${}_{1}H^{1}$ to ${}_{92}U^{238}$. In all but two of these naturally occurring nuclei, the number of neutrons is equal to the number of protons or somewhat larger. As the number of protons increases, the excess number of neutrons tends also to increase as can be seen in the sequence of the nuclei of ${}_{2}He^{4}$, ${}_{9}F^{19}$, ${}_{83}Bi^{209}$, and ${}_{92}U^{238}$. In the case of most atoms, the ratio of the number of neutrons to the number of protons is not rigidly fixed. More usually the number of neutrons is variable within a small range and nuclei occur commonly with the same charge but with different masses. Such nuclei are called "isotopes" of one another (from the Greek, meaning "same place," applying to same place in the Periodic Table of elements). Since the num-

ber of orbital electrons is the same for all members of a set of isotopes, the chemical properties are identical. Most naturally occurring elements are a mixture of isotopes, which accounts for the fact that atomic weights are seldom integers.

Table 118 offers a brief summary of the properties of the nucleus and its components. It should be noted that in atomic and nuclear physics, the mass unit chosen is one-sixteenth of the mass of the predominant oxygen isotope, ${}_8O^{16}$, and is equal to 1.6603×10^{-24} g, which is greater than the value used by chemists by a factor of 1.00027.

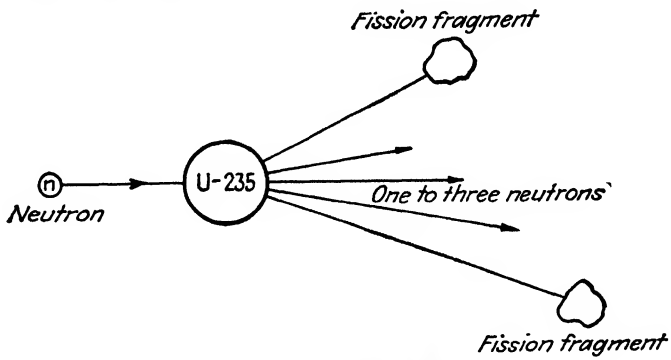


FIG. 364. Fission of ${}_{92}U^{235}$.

TABLE 118. SOME PROPERTIES OF THE NUCLEUS AND ITS COMPONENTS

	Nucleus	Proton (${}_1H^1$)	Neutron (${}_0n^1$)
Mass, units.....	About $A \times 1.0083$	1.00758	1.00893
Diameter, cm . .	About 10^{-12}	10^{-13}	10^{-13}
Density, g per cc.	10^{14}	10^{14}	10^{14}
Charge, coulombs.	$Z \times 1.6 \times 10^{-19}$	1.6×10^{-19}	0
Number in nucleus		Z	$A-Z$

More detailed information giving the nuclear properties of the various species of atoms can be obtained by referring to the Segre chart.[4]

The Fission Process. Physicists during the nineteen twenties had come to realize the fundamental concept that mass and energy are interchangeable. Einstein's relation $E = mc^2$ (where E is the amount of energy equivalent to a mass m and c is the velocity of light) is the basis for all considerations of nuclear power generation. It was not until 1932, however, that experimental proof of this relation was realized. At that time Rutherford's workers showed that by bombarding a target of lithium with protons (${}_1H^1$ nuclei) of 700 kv energy the following occurred:[2]

$${}_3Li^7 + {}_1H^1 \rightarrow {}_2He^4 + {}_2He^4$$
$$\text{Mass } 8.0241 \rightarrow 8.0056$$

It was evident that 0.0185 units of mass had disappeared in the reaction. The energy of each α-particle ($_2He^4$ nucleus) was found to be 8.5 million electron volts Mev* or a total energy release of 17 Mev. Since 0.0185 units of mass is 3.07×10^{-26} gm, 17 Mev is 27.2×10^{-6} erg and c is 3×10^{10} cm per sec, by substituting in the equation

$$\begin{aligned} E &= mc^2 \\ 27.2 \times 10^{-6} &= 3.07 \times 10^{-26} \times 9 \times 10^{20} \\ &= 27.6 \times 10^{-6} \end{aligned}$$

or substantial equivalence.

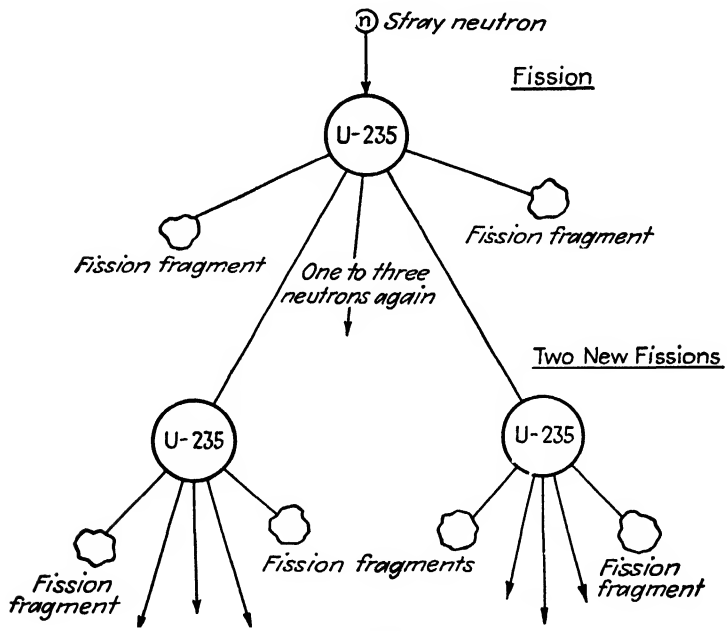


FIG. 365. Chain reaction of $_{92}U^{235}$ without moderator.

The heavy atoms have nuclei which approach instability and under certain conditions can be made to split into two fragments, with the loss of some neutrons so that in the process mass is lost and energy is released. For example if a neutron ($_0n^1$) strikes a nucleus of $_{92}U^{235}$ two fragments will

* *One* electron volt (ev) is defined as being equal to the kinetic energy that a particle carrying *one* electronic charge acquires in falling freely between a potential drop of *one* volt. For convenience this value is multiplied by one million, hence Mev. Further to exemplify the energy unit Mev it can be shown that 1 Mev = 1.6×10^{-6} erg and that 3.6×10^{13} ergs = 1 kw-hr.

be formed as shown in Fig. 364, together with from one to three neutrons, yielding a total energy release of about 200 Mev.

If only a small percentage of the released neutrons is captured before they can strike another nucleus of $_{92}U^{235}$, then the possibility is at hand to form a self-perpetuating cycle—the chain reaction (Fig. 365).

From the chain reaction it can be shown that, since each fission yields 200 Mev which is equal to 3.2×10^{-4} erg, or 3.1×10^{-14} Btu, or 8.9×10^{-18} kw-hr, and since a pound of $_{92}U^{235}$ contains 11.7×10^{23} atoms or nuclei, 1 lb of the isotope $_{92}U^{235}$ upon fission produces about 4×10^{10} Btu. Since

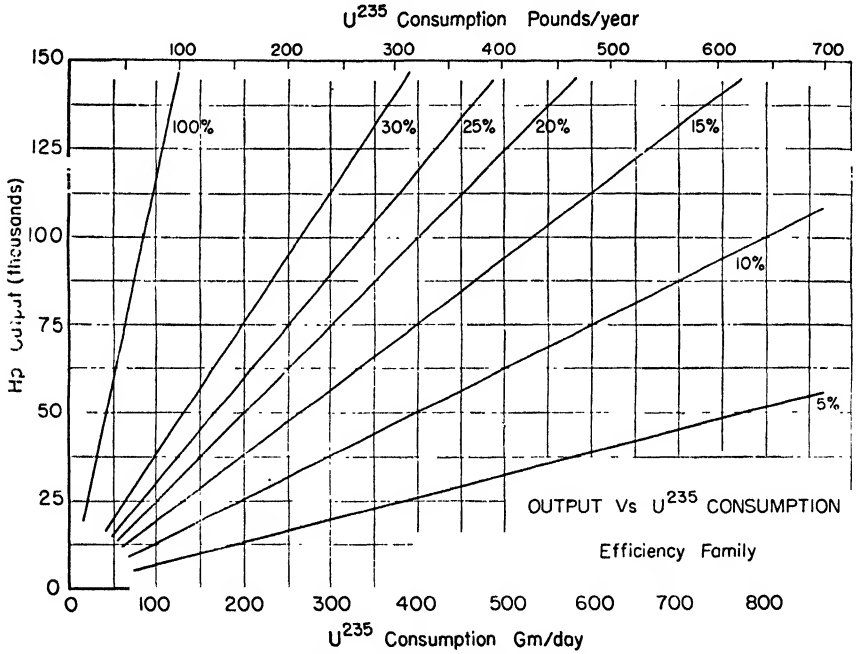


FIG. 366.[4] Power available from U^{235}.

1 lb of good coal yields only 14,000 Btu, 1 lb of fissionable $_{92}U^{235}$ is equivalent to approximately 1,500 tons of coal. Figure 366 shows graphically the horsepower outputs available with various rates of consumption from fission of $_{92}U^{235}$ under seven different operating efficiencies. Therefore, $_{92}U^{235}$ is potentially a highly concentrated fuel, which may in the future partly displace coal and oil now utilized in present-day power installations.

It should be noted that $_{92}U^{235}$ is not the only fissionable material which could be used as fuel. Plutonium ($_{92}U^{239}$), which is made from natural uranium, and the isotope of uranium ($_{92}U^{233}$), which is made from thorium, are also possible fuels.

Turning again to the energy release from the fission process, it can be shown to be proportioned roughly as follows:

	Million Electron Volts
Fission fragments	160
Neutrons (prompt)	5
Gammas (prompt)	4
Radioactive series	20
Absorbed neutrons	9
Total	198

In fission induced by thermal neutrons, the nucleus seldom splits exactly in half, as one part is usually heavier than the other, giving an average distribution of new atoms as shown by the curve[4] in Fig. 367.

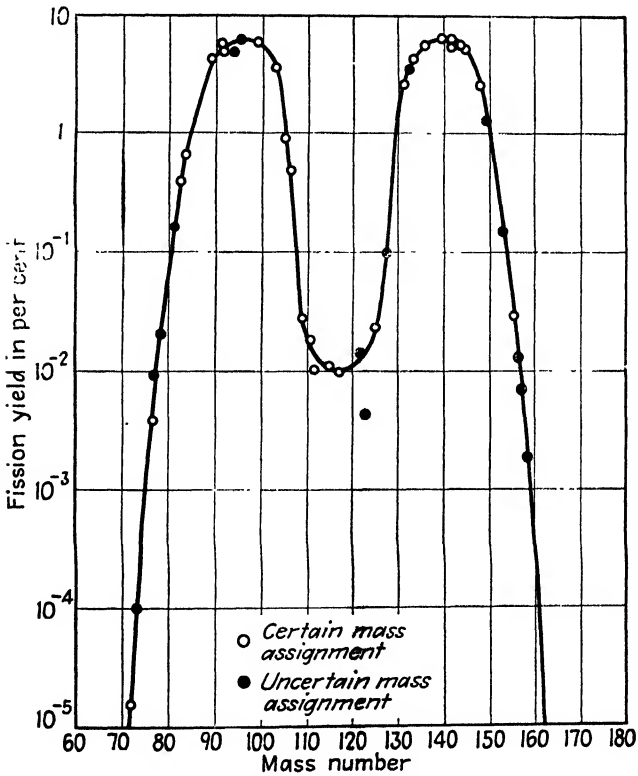


FIG. 367. Fission product curve[4].

The interactions between bombarding neutrons and nuclei are expressed very simply in terms of nuclear cross sections. The meaning of the cross section of a given species of nucleus is best understood if we imagine a beam of neutrons of a given energy bombarding the nucleus; a certain fraction of

the neutrons will be removed from the beam by the nucleus. By definition, the fraction of neutrons contained in a 1 sq cm beam that is intercepted by a single nucleus is called the total cross section (σ) of the particular nucleus for such neutrons. Thus, in essence, the cross section is a measure of the probability that an incoming neutron will interact with the nucleus which is being bombarded. The atomic electrons play an insignificant role in these interactions.

The total cross section is composed of separate contributions from the various processes that may occur. For instance, the bombarding neutron may be absorbed into the nucleus in a certain fraction of the events. This cross section is usually denoted by σ_a. However, there is always a certain chance that the incoming neutron will be merely scattered off the nucleus without being absorbed. The probability for this process is represented by the scattering cross section σ_s. Consider, for instance, the collision of neutrons with hydrogenous material. In this case, only absorption and scattering can occur, and therefore the total cross section is expressed by $\sigma = \sigma_a + \sigma_s$.

The scattering process can be subdivided further, such as by considering whether or not the scattered neutron has lost a significant fraction of its original energy. If it has, we speak of inelastic scattering, otherwise, of elastic scattering. In this discussion, we shall not find it necessary to use special symbols for these cross sections.

In the case of fissionable nuclei, we may define σ_f, the cross section for fission which is a measure of the probability that an incident neutron will cause fission of the nucleus.

The probability that a certain process occurs varies with the energy of the incoming particle. Hence, the separate cross sections vary with energy, and therefore the total cross section is also a function of energy. For instance, it is found that if ${}_{92}U^{238}$ is bombarded with neutrons of varying energy, σ_a shows a very marked energy dependence. In particular, there are certain energies at which the absorption is extraordinarily high—we then speak of a resonance process. For ${}_{92}U^{238}$ this occurs at comparatively low energies.

Neutrons that are emitted in the fission process are emitted with an average energy in the Mev region. Thus, for this discussion we speak of such neutrons as fast neutrons. If these neutrons are slowed down by losing energy in collision, they eventually move with kinetic energy equivalent to the temperature of the surroundings. It is easily calculated that room temperature corresponds to $\frac{1}{40}$ ev. Thus we speak of neutrons that possess an energy of the order of 10^{-1} ev as "thermal neutrons."

The energy of the bombarding neutrons should always be borne in mind when the values for cross sections of refractory or other material are quoted.

More specifically, in case a certain material has a high-absorption cross section, the total cross section is primarily due to absorption. Therefore $\sigma = \sigma_a$, such as is the case for boron. In other materials, such as bismuth, the total cross section is almost entirely due to scattering. Hence, $\sigma = \sigma_s$. Many materials, however, possess nuclear properties such that both absorption and scattering play an important role, and we must consider that $\sigma = \sigma_a + \sigma_s$. The dimensions for each of these cross sections, as the name implies, are area per nucleus, usually expressed as square centimeters per nucleus. Because most of these cross sections are in the order of 10^{-24} sq cm per nucleus in magnitude, this area has been nicknamed the "barn"; *i.e.*, 1 barn = 10^{-24} sq cm per nucleus. An example of the large differences that can exist between somewhat similar nuclei both bombarded with thermal neutrons is as follows:

$$\sigma_a({}_1H^1) = 0.31 \text{ barn}$$
$$\sigma_a({}_1H^2) = 0.00065 \text{ barn}$$

For most elements, the sizes of nuclear cross sections cannot be accurately predicted from present theoretical knowledge but are obtained from a variety of experimental determinations.

Table 119 indicates the effect of various nuclei on the bombarding thermal neutrons. It must be emphasized that only a trace of some elements such as boron will so limit the production of neutrons that the chain reaction cannot be sustained. For this reason, extremely high purity is required in many components of nuclear power plants. Refractory materials considered for these applications not only must be examined beforehand for the effects of major chemical constituents on the bombarding neutrons but must also be analyzed spectrographically or otherwise for microquantities of elements that could, perhaps, seriously affect the desired nuclear reaction. Cross sections for nuclei-bombarded neutrons at higher energy levels may be found from curves.[4]

In order to produce a self-sustaining chain reaction, it is evident that the number of neutrons available in the fuel (or fissionable material) must be utilized in the most efficient way. In any nuclear power production reactor, there are essentially three processes competing for these neutrons. They are

1. The absorption of neutrons by the fissionable material, which results in fission and hence more neutrons, which sustain the chain reaction.
2. The nonfission absorption by the materials in the reactor, such as the moderator material, reflectors, impurities in these materials, etc.
3. The escape of neutrons from the system.

Therefore, the condition for obtaining such a chain reaction must be such that the number of neutrons produced by fission must be equal to or slightly

TABLE 119. SOME NUCLEAR PROPERTIES OF THE ELEMENTS[4]

Atomic number Z	Element	Density		Chemical at. wt	Nuclei per cc, N × 10^{24}	Nuclear cross sections, barns			Cross section, cm^{-1}	
		g per cc	At T,°C			σ	σ_s	σ_a	$N\sigma_c$	$N\sigma_a$
1	H	0.0709	−252.7	1.0078	0.0424	20	0.30	20	0.013	0.85
2	He	0.126	−268.9	4.003	0.0190	1.5	0	1.5	0	0.029
3	Li	0.53	20	6.940	0.0459	66.3	64	2	2 9	0.092
4	Be	1.8	20	9.02	0.120	6.1	0.009	6.1	0 0011	0.73
5	B	2.3	20	10.82	0.139	703	700	3	97	0.42
6	C	1.62	20	12.01	0.0805	4.84	0.0045	4.8	0 00036	0.39
7	N	0.808	−195.8	14.008	0.0347	11.75	1.75	10	0 061	0.35
8	O	1.14	−183	16.000	0.0429	4.1	0.0016	4.1	0 000068	0.18
9	F	1.11	−187	19.00	0.0351	4.1	0.065	4.1	0.0023	0.14
10	Ne	0.9002		20.183	0.0268	2.8		~2.5		0.067
11	Na	0.93	97.5	22.997	0.0243	4	0.5	3.5	0 012	0.085
12	Mg	1.57	650	24.32	0 0389	4	0.4	3.6	0 016	0.14
13	Al	2.4	658	26.97	0.0536	1.7	0 23	1 5	0 012	0 080
14	Si	2.4	20	28 06	0.0515	1.95	0.25	1.7	0 013	0 088
15	P	1.745	44.5	30.98	0.0339	10.3	0.31	10	0.01	0.34
16	S	1.808	115	32.06	0.0339	2	0.53	1.5	0.018	0.051
17	Cl	1.557	−33.6	35.457	0 0264	<43	33	~10	0 87	~0 26
18	A	1.402	−185.7	39.944	0.0211	2.53	0 62	1.9	0 013	0 040
19	K	0.83	62	39.096	0.0128	3.7	2.2	1.5	0 028	0 010
20	Ca	1.55	20	40.08	0.0233	9.93	0.43	9.5	0 01	0.22
21	Sc	2.5	20	45.10	0.0334		2.8		0.094	
22	Ti	4.5	20	47.90	0.0566	11.2	5.2	6	0.29	0.34
23	V	5.68	20	50.95	0.0704	>13	6	>7	0.42	>0.49
24	Cr	7.14	20	52.01	0.0822	6.5	3	4	0 25	0.33
25	Mn	7.2	20	54.93	0.0789	15.2	12.8	2.4	1.01	0.19
26	Fe	6.9	1530	55.85	0.0744	12	2.5	11	0.19	0.82
27	Co	8.9	20	58.94	0.0909	38	33	5	3.0	0.45
28	Ni	8.90	20	58.69	0 0913	17.4	4.4	18	0.40	1.6
29	Cu	8.3	1083	63.57	0 0786	11.2	4	8	0.31	0.63
30	Zn	6.7	463	65.38	0.0617	4.85	1.25	4.2	0.077	0.26
31	Ga	5.91	20	69.72	0.0510	20	2.3	18	0.12	0.92
32	Ge	5.36	20	72.60	0.0444	25	~0.6	22	~0 03	0.98
33	As	2.0	20	74.91	0.0161	12.6	5.6	7	0.09	0.11
34	Se	4.50	25	78.96	0 0343	28	16	10	0 55	0.34
35	Br	3.119	20	79.916	0.0235	9.5	2.5	7	0.059	0.16
36	Kr	(2)		83.7	0.0144	27	0.1	27	0.001	0.39
37	Rb	1.53	20	85.48	0 0104	12	0.5	11	0.005	0.11
38	Sr	2.6	20	87.63	0 0179	11	1.5	10	0 027	0.18
39	Y	5.51	20	88.92	0.0373		1.1		0.041	
40	Zr	6.4	20	91.22	0.0422	15	>0 5	14	>0.021	0.59
41	Cb	8.57	20	92.91	0.0555	6.9	1.4	5	0.078	0.28
42	Mo	10.2	20	95.95	0.0638	7.9	3.9	6.5	0.25	0.41
43	Tc			99						
44	Ru	12.2	20	101.7	0.0502			6		0.30
45	Rh	12.5	20	102.91	0.0496	155	150	5	7.4	0.25
46	Pd	11	1550	106.7	0.0639	13.5	9	4.5	0.58	0.29
47	Ag	10.5	20	107.880	0.0567	66.4	58.5	6.6	3.3	0.37
48	Cd	8.6	20	112.41	0.0461	2507.2	2500	5.3	115	0.24
49	In	7.3	20	114.76	0 0383	194	190	4	7.3	0.15
50	Sm	5.750	20	118.70	0.0292	4.89	0.69	5.0	0.020	0.15

TABLE 119. SOME NUCLEAR PROPERTIES OF THE ELEMENTS (*Continued*)

Atomic number Z	Element	Density		Chemical at. wt	Nuclei per cc, $N \times 10^{24}$	Nuclear cross sections, barns			Cross section, cm^{-1}	
		g per cc	At T,°C			σ	σ_c	σ_s	$N\sigma_c$	$N\sigma_s$
51	Sb	6.68[d]	25	121.76	0 0330	9	4.7	4.2	0.155	0.14
52	Te	(β)6.00	20	127.61	0 0283	10	5	5	0 14	0 14
53	I	4 93	20	126.92	0 0234	9.4	6.8	3	0 16	0.07
54	Xe	(2.7)		131.3	0.0124	35				
55	Cs	1.90	20	132.91	0.0086	50	41	9	0 35	0 08
56	Ba	3.5	20	137.36	0.0153	9 25	1 25	8	0 019	0.12
57	La	6.15	20	138 92	0 0267	25	12	13	0.32	0 35
58	Ce	6.9	20	140 13	0 0296	29				
59	Pr	6.50	20	140.92	0 0278	>25				
60	Nd	6.90	20	144.27	0.0288		90		2.6	
61	Pm			147						
62	Sm	7.7	20	150 43	0.0308		8,000		246	
63	Eu			152 0			2,500			
64	Gd			156.9			~38,000			
65	Tb			159.2		15				
66	Dy			162.46			850			
67	Ho			164 94			65			
68	Er			167.2			200			
69	Tm			169.4			130			
70	Yb			173.04		65				
71	Lu			174.99			195			
72	Hf	11 4	20	178 6	0 0384	130	120	10	4 6	0 38
73	Ta	16 6	20	180.88	0 0552	24.5	35	7.2	1 93	0.40
74	W	19.3	20	183 92	0 0631	20.9	16	5.7	1 01	0 36
75	Re	20	20	186.31	0 0691		130		9.0	
76	Os	22 48	20	190 2	0 0707	30	20	10	1.41	0 71
77	Ir	22.4	20	193 1	0 0699		400		27.9	
78	Pt	19	17.55	195 23	0 0586	21.5	10.8	12	0.63	0.70
79	Au	19.3	20	197.2	0 0589	101	94.5	5	5.57	0.29
80	Hg	14.19	−38.9	200.61	0 0426	440	425	15	18.1	0 64
81	Tl	11.85	20	204.39	0 0349	16 9	2.9	9.7	0.101	0.34
82	Pb	11.34	20	207 21	0 0329	10 2	0.17	13	0 006	0.43
83	Bi	9.8	20	209.00	0.0282	8 9	0 016	9 2	0 0005	0.26
84	Po			210						
85	At			211						
86	Rn	4.40	20	222	0.0108					
87				223						
88	Ra	5.0	20	226.05	0 0133					
89	Ac			227						
90	Th	11.5	20	232.12	0.0290	16	6	~10	0.17	~0.29
91	Pa			231						
92	U	18.7	20	238.07	0.0473	10	~2	8.2	0.095	0.39
93	Np			237						
94	Pu			239						
95	Am			241						
96	Cm			242						

the plutonium can be extracted from the uranium by chemical methods, since the two elements are chemically dissimilar. Therefore, the possibility is at hand to use all the natural uranium as fuel and not be limited to the 0.7 per cent of $_{92}U^{235}$ in natural uranium, provided that the source of chain-reacting neutrons is replenished. However, the material in the pile must be periodically reprocessed to remove all the fission fragments that

FIG 369. World sources of fissionable materials. (*Courtesy of Fortune Magazine.*)

tend to add further to the capturing nuclei present in the pile and therefore lower the reactivity.

The other secondary fuel is $_{92}U^{233}$. This isotope can be made synthetically if $_{90}Th^{232}$ is incorporated in the primary nuclear reactor as described for the production of plutonium. The reaction is as follows:

$$_{90}Th^{232} + {}_{0}n^{1} \cdot \quad \cdot\, {}_{90}Th^{233} \xrightarrow[23\ \text{min}]{\beta^-} {}_{91}Pa^{233} \xrightarrow[27\ \text{days}]{\beta^-} {}_{92}U$$

Although no technological details are available in regard to $_{92}U^{233}$, it is known that it undergoes fission with thermal neutrons and for this reason is also a potential nuclear fuel.

The maps (Figs. 369) offer some pertinent facts about the availability of fuels.

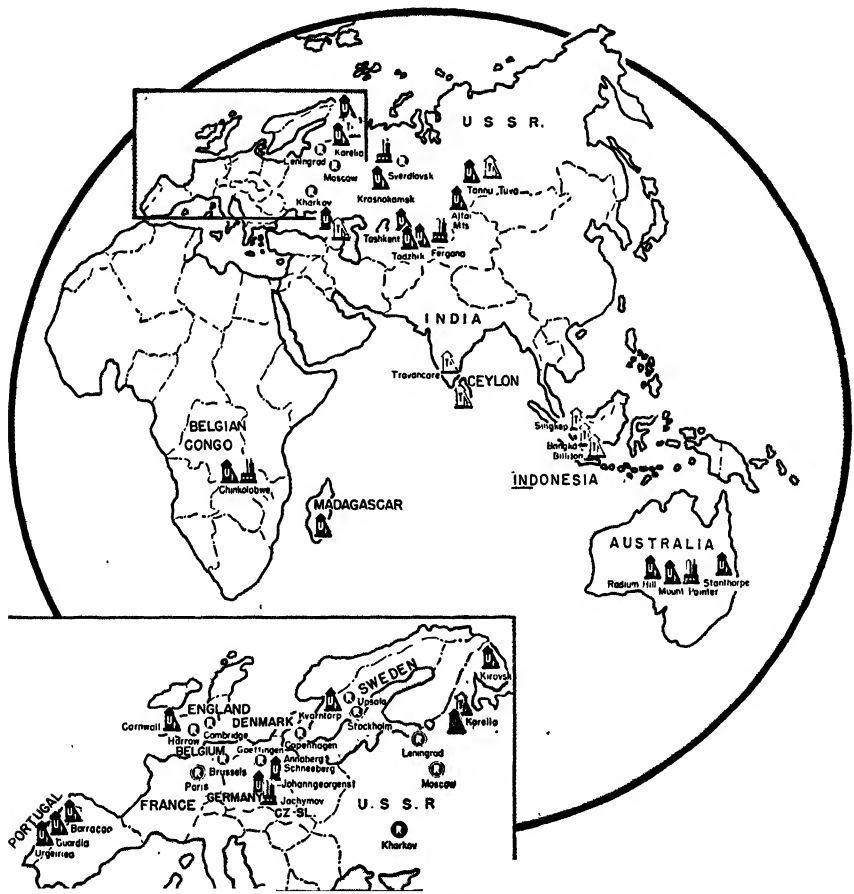


FIG. 369 *(Continued)*

4. Design of Power Piles or Reactors. The energy obtained from nuclear fission can be made available in the form of heat within the pile, or reactor. Before describing the actual designs of reactors that have been made and possible future designs of reactors for power purposes, it might be well to discuss how the heat from the pile, or reactor, can be utilized. Many impractical suggestions have been made, but apparently the only one that has a firm basis utilizes a circulating fluid, either liquid or gas,

which passes through the reactor operated at a finite temperature level. The hot fluid is then sent through a heat exchanger where water is converted to steam, which is used to run a turbine, or where the hot fluid in the form of a vapor or gas can be used to drive a high-temperature gas turbine. It is necessary to work at the highest temperature level for good efficiency. The failure of materials to stand up at high temperatures is the most important limiting factor. Refractory materials, such as high-melting-point oxides,

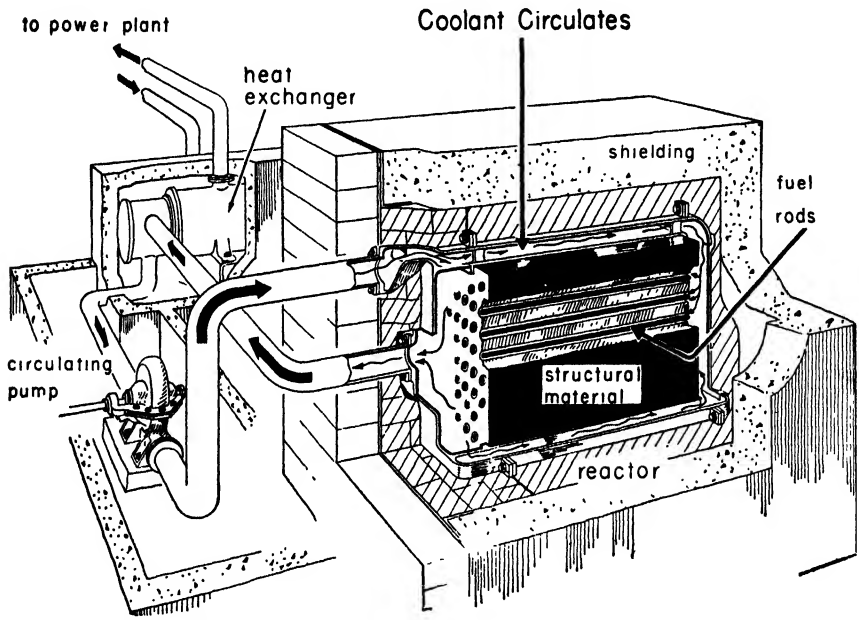


FIG 370. Heterogeneous reactor with solid diluent and circulating coolant.(o)

seem to be most encouraging owing to their stability and strengths at elevated temperatures.

Reactors are considered to be of two classes: heterogeneous and homogeneous. In the heterogeneous reactor, the fissionable material is in rods or lumps such as was described for the pile used in the production of plutonium from natural uranium. In the homogeneous reactor, the fissionable material may be used in pure, metallic form, in metallic alloy form, or in the form of a solution or intimate mixture with a diluent.

Each of these two classes of reactors can be of three general types: fast, intermediate, or thermal—so named for the average energy of the neutrons that propagate the chain reaction.

The fluid or material used for the transferring of heat from the reactor

to the prime mover must possess the best over-all properties that satisfy the following conditions:

1. Must possess good nuclear properties; small absorption cross section and, in some cases, high moderating power.
2. Must be able to withstand high temperatures.
3. Must possess high heat transfer values.
4. Must not be made highly radioactive in the reactor.
5. Must not corrode or react with other materials in the reactor

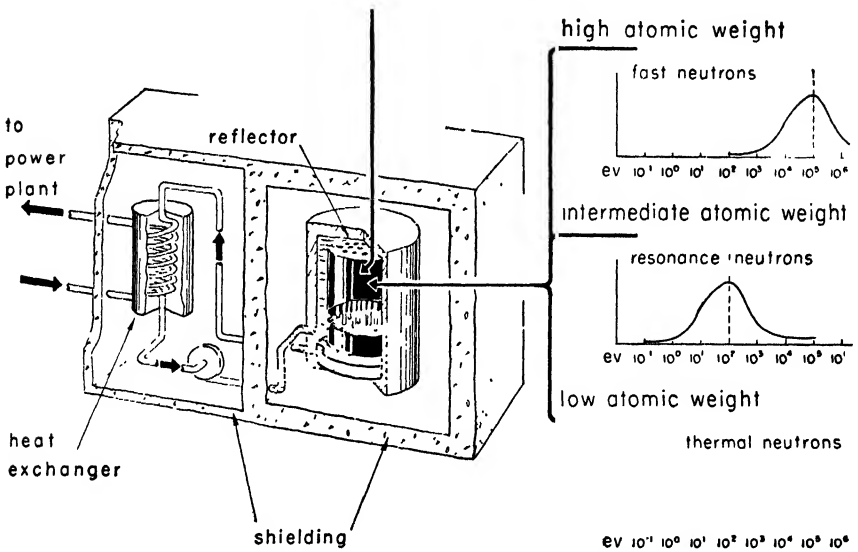


FIG. 371. Schematic diagram of a homogeneous reactor containing a solid fuel mixture. The cylindrical core or central section consists of a high-melting-point mixture of U or Pu.[4]

Materials that have been suggested are gases such as helium and air, liquids such as water and liquid metals, and homogeneous mixtures of the fuel itself dissolved or suspended in a liquid. The general heat-transfer problems are discussed by E. R. Gilliland.[4]

Table 120 is a summary of nuclear reactors that have been built thus far. None of the piles, or nuclear reactors, have been used for the production of useful, peacetime power. The Hanford-type pile as was mentioned previously is a primary reactor used to produce plutonium and is cooled by water, not to produce subsequent useful power, but to prevent the overheating of the pile. The Alamogordo, Hiroshima, Nagasaki, and Bikini fast reactors were military weapons, which liberated a vast amount of energy in extremely short intervals of time.

To form a reactor that can be used for the production of useful power, we have a number of possibilities, which are clearly discussed by Fermi.[3]

TABLE 120. SUMMARY OF NUCLEAR REACTORS[4]
Described in Open Literature

Location	Initial dates	Class	Type	Fissionable material	Moderator	Coolant	Power developed or energy released	Reference
University of Chicago. (West Stands)	Dec. 2, 1942	Heter.	Thermal	U + U oxide (lumps)	Graphite	None	200 watts	(1)
Oak Ridge	Nov. 4, 1943	Heter.	Thermal	U (Al-clad rods)	Graphite	Air	>2000 kw	(2)
Argonne	Spring, 1943	Heter.	Thermal	U + U oxide (lumps)	Graphite	None	Few kw	(3)
Hanford (three)	Summer, 1944–Spring, 1945	Heter.	Thermal	U (Al-clad rods)	Graphite	Water	$\gg 10^3$ kw	(4)
Argonne	May 15, 1944	Heter.	Thermal	U (rods)	D_2O	D_2O	>300 kw	(5)
Los Alamos	1944 ?	Homo.	Thermal	Enriched U	H_2O	H_2O	10 kw	(6)
Chalk River	Fall, 1945	Heter.	Thermal	U (rods)	D_2O	D_2O	3.5 watts	
Alamogordo	July 16, 1945	Homo.	Fast	U-235 or Pu-239	None	None	$>10^5$ tons TNT	(7)
Hiroshima	Aug. 6, 1945	Homo.	Fast	U-235 or Pu-239	None	None	$>10^5$ tons TNT	(8)
Nagasaki	Aug. 9, 1945	Homo.	Fast	U-235 or Pu-239	None	None	$>10^5$ tons TNT	(8)
Bikini (two)	July 1 and July 25, 1946	Homo.	Fast	U-235 or Pu-239	None	None	$>10^5$ tons TNT	(8)
Haigerloch, Germany.	?	Heter.	Thermal	U (2 tons)	D_2O(2 tons) C (10 tons)	?	?	(9)
Los Alamos	Sept. 6, 1947	Homo.	Fast	Pu-239	None	?	?	(10)

References:

Smyth report (1): Section 6.29 and Appendix 4; (2): Sections 6.44, 8.37, 8.43, 8.53; (3): 8.28; (4): Sections 7.19, 8.53; (5): 8.27, 8.32; (7): Appendix 6.
(6): R. F. Christy, verbal report Chicago meetings, American Physical Society, July, 1946. *Abstract Bull. Am. Phys. Soc.*, December, 1946.
(8): *Chem. Eng. News*, pp. 1782–1786, July 10, 1946; *Life*, pp. 25–29, July 15, 1946; *Power*, pp. 83–91, September, 1946.
(9): Quotation from W. Heisenberg, *Boston Herald*, Feb. 24, 1947.
(10): Science News Letter, Sept. 6, 1947.

Results indicate that natural uranium cannot be used for fuel in a self-sustaining *homogeneous* thermal reactor unless heavy water is used as a moderator. It can, however, be used as a fuel in a self-sustaining *heterogeneous* reactor using graphite as a moderator such as was mentioned for the production of plutonium in the Hanford piles. Figures 370 and 371 are proposed designs for a heterogeneous and homogeneous reactor, respectively.

In the case of the *homogeneous* reactor, the cylindrical core, or central section, could consist of a high-melting-point mixture of plutonium or uranium with a selected diluent. An alloy or a simple mechanical mixture of metal or compound with a diluent might be used. The core could be fabricated in sections or as a subcritical whole. It should be possible to obtain sufficient excess reactivity for operation from the introduction of the coolant and the addition of a reflector or material having a high scattering cross section. The coolant used could be either liquid or gas. Table 121 lists some possibilities for the components of a reactor when enriched uranium is considered as the fuel.

In the case of the *heterogeneous* reactor, the fuel rods, clad with a non-corrosive metallic coating, could be mounted horizontally in a structural

TABLE 121. SUMMARY OF MATERIALS OF CONSTRUCTION FOR HOMOGENEOUS NUCLEAR REACTORS THAT MIGHT OPERATE AT VERY HIGH TEMPERATURES[4]

Enriched Uranium Assumed in Each Case

Type	Reactor materials	Mp, °C	Reflector		Limitations
			Materials	Max. T_s,°C	
Fast*.....	U	1150	W	3370	Oxidation of W
Fast*.....	U + W	<3370	W	3370	Oxidation of W and U
Fast*.....	U	1150	C	3500	Oxidation of C
Fast*.....	U + Th	<1150	ThO_2	>3000	
Resonance.. .	U + Ta	?	Ta	2800	Oxidation of Ta
Resonance....	U + Re	<1150	Re	3400	Scarcity of Re
Resonance.. .	U + Cu	<1150	MgO	2800	
Resonance....	U + Cu	<1150	ThO_2	>3000	
Resonance....	U + MgO	?	MgO	2800	
Thermal.....	U + Be	<1150	BeO	2600	
Thermal.....	U + BeO	?	BeO	2600	Thermal stresses
Thermal.....	UC_2	2260	C	3500	Oxidation of C
Thermal.....	U + C	?	MgO	2800	
Thermal.....	UO_2	2500	MgO	2800	
Thermal.....	U + Be_2C	?	Be_2C	2100	Decomposition of Be_2C
Thermal.....	U + Al_2O_3	?	Al_2O_3	2500	

* Assumed to operate with molten core.

material that serves as a moderator in a thermal unit or as a diluent in a resonance or fast unit. A removable section of shielding allows the end manifold to be removed for replacement of fuel and other parts. Because of the intense radiations, this work would have to be accomplished by remote-controlled devices. The coolant would probably be a liquid; however, for special cases a gas coolant could probably be used whereby a

TABLE 122. SOME HIGH-MELTING-POINT COMPOUNDS OF URANIUM

Material	Melting Point, °C
U	About 1150
UO_2	2180
U_2C_3	2400
UN	?
UB	?
US	Above 2000
U_2S_3	1850
US_2	1850

TABLE 123. ELEMENTS HAVING LARGE ABSORPTION CROSS SECTIONS[4] For Thermal Neutrons

Materials	Atomic No. Z	Nuclear cross sections, barns		
		σ	σ_a	σ_s
Lithium	3	66.3	64	2
Boron	5	703	700	3
Manganese	25	15.2	12.8	2.4
Cobalt	27	38	33	5
Rhodium	45	155	150	5
Silver	47	66.4	58.5	6.6
Cadmium	48	2,507.2	2,500	5.3
Indium	49	194	190	4
Cesium	55	50	41	9
Samarium	62		8,000	
Europium	63		2,500	
Gadolinium	64		38,000	
Dysprosium	66		850	
Holmium	67		65	
Erbium	68		260	
Thulium	69		130	
Lutecium	71		195	
Hafnium	72	130	120	10
Tantalum	73	24.5	35	7.2
Rhenium	75		130	
Iridium			400	
Gold	79	101	94.5	5
Mercury	80	440	425	15

substantially larger proportion of the reactor volume would be required for the coolant.

5. Survey of Refractories for Potential Use in Power Reactor Development. Refractory materials may find application in the following four major components of the pile:

1. Fuel
2. Control rods
3. Reflector
4. Moderator

Refractories for Fuel. In some types of homogeneous and heterogeneous reactors, it may be necessary to use pure metallic fissionable materials for fuel. As was mentioned before, at elevated temperatures these reactors would operate with a molten core. In some types of reactors, it may be desired to maintain the fuel in solid form at elevated temperatures. Table 122 suggests some of the possible high-melting-point compounds of uranium and its isotopes.

Refractories for Control Rods. Control rods are very important in that their function is to absorb the excess of neutrons in the chain reaction in the reactor. If the number of neutrons available for creating additional fis-

TABLE 124. SOME HIGH-MELTING-POINT COMPOUNDS* OF LARGE-ABSORPTION CROSS-SECTION ELEMENTS
For Thermal Neutrons

Material	Formula	Melting point, °C
Lithium oxide	Li_2O	1700
Boron	B	2300
Boron carbide	B_4C	2350
Boron nitride	BN	2730
Manganese oxide	MnO	1790
Cobalt oxide	CoO	1800
Rhodium	Rh	1950
Indium oxide	In_2O_3	2000
Hafnium	Hf	1700
Hafnium oxide	HfO_2	2810
Hafnium carbide	HfC	3530
Hafnium nitride	HfN	3307
Tantalum	Ta	2850
Tantalum oxide	Ta_2O_5	1875
Tantalum carbide	TaC	3880
Tantalum nitride	TaN	3087
Rhenium	Re	3000
Samarium sulfide	Sm_2S_3	1900

* Most of the elements and/or compounds thereof except for the oxides could *not* be maintained at elevated temperatures in normal atmospheres.

sions was not controlled, the chain reaction would get out of hand and the reactor components would melt and contaminate a large area with highly radioactive material. Therefore, it may be said that the control rods govern the pile temperature. A control-rod should have a high absorption cross section as well as high chemical and physical stability at high temperatures. Table 123 lists the elements that possess large absorption cross sections. Table 124 lists some high-melting-point compounds of these elements which could perhaps be used as control rods. On the other hand,

TABLE 125. ELEMENTS POSSESSING LARGE SCATTERING CROSS SECTIONS[4] For Thermal Neutrons

Material	Atomic No. Z	Nuclear σ	Cross sections, barns	
			σ_a	σ_s
Hydrogen	1	20	0.30	20
Helium	2	1.5	0	1.5
Beryllium	4	6.1	0.009	6.1
Carbon	6	4.84	0.0045	4.8
Nitrogen	7	11.75	1.75	10
Oxygen	8	4.1	0.0016	4.1
Fluorine	9	4.1	0.065	4.1
Sodium	11	4	0.5	3.5
Magnesium	12	4	0.4	3.6
Phosphorus	15	10.3	0.31	10
Calcium	20	9.93	0.43	9.5
Iron	26	12	2.5	11
Nickel	28	17.4	4.4	18
Zinc	30	4.85	1.25	4.2
Gallium	31	20	2.3	18
Germanium	32	25	0.6	22
Bromine	35	9.5	2.5	7
Krypton	36	27	0.1	27
Rubidium	37	12	0.5	11
Strontium	38	11	1.5	10
Zirconium	40	15	0.5	14
Columbium	41	6.9	1.4	5
Ruthenium	44			6
Tin	50	4.89	0.69	5.0
Barium	56	9.25	1.25	8
Thallium	81	16.9	2.9	9.7
Lead	82	10.2	0.17	13
Bismuth	83	8.9	0.016	9.2
Thorium*	90	16	6	10
Uranium*	92	10	2	8.2

* Thorium and uranium might be used as reflectors. There would be the possibility of forming secondary fuels in the process.

control rods may be cooled so that lower temperature materials may be used.

Refractories for Reflectors. The layer of material immediately surrounding the reactor is of great importance in preventing the escape of neutrons, for it is evident that the excessive escape of neutrons would reduce the efficiency of the reactor. Reflector materials should possess a large scattering cross section. Table 125 lists some of the elements possessing large

TABLE 126. SOME HIGH-MELTING-POINT COMPOUNDS OF LARGE SCATTERING CROSS-SECTION ELEMENTS
For Thermal Neutrons

Material	Formula	Melting point, °C
Beryllium oxide	BeO	2520
Beryllium carbide	Be_2C	2100 decomposes
Beryllium nitride	Be_3N_2	2200
Carbon	C	3500
Magnesium oxide	MgO	2800
Magnesium sulfide	MgS	2000
Calcium oxide	CaO	2570
Iron	Fe	
Iron oxide	Fe_2O_3	1550
Nickel	Ni	1960
Nickel oxide	ZnO	1980
Zinc oxide	Ga_2O_3	1740
Gallium oxide	SiO	2430
Strontium oxide	SrS	2000
Strontium sulfide	Zr	1900
Zirconium	ZrO_2	2720
Zirconium oxide	ZrC	2750
Zirconium carbide	ZrN	2982
Zirconium nitride	Cb	1955
Columbium	Cb_2O_5	1520
Columbium oxide	CbC	3770
Columbium carbide	CbN	2050 decomposes
Columbium nitride	Ru	2450
Ruthenium	SnO_2	1900
Tin oxide	BaO	1920
Barium oxide	Th	1845
Thorium	ThO_2	3050
Thorium oxide	ThC_2	2773
Thorium carbide	ThS	1925
Thorium sulfide	UC_2	2260
Uranium carbide	U_2C_3	2400
Uranium nitride	UN	
Uranium sulfide	US	

scattering cross sections, while Table 126 lists some of the elements possessing large scattering cross sections and compounds thereof that have high melting points.

Refractories for Moderators. A moderator must be made of a material having light nuclei and a low-absorption cross section. Table 127 is a

TABLE 127. COMPARISON OF LIGHT ELEMENTS AS MODERATORS[4]
The Values Given Are for Thermal Energies

Element	A	Cross section, cm		§	Slowing-down power $N\sigma_s$§	Moderating ratio $\frac{\sigma_s}{\sigma_c}$§
		Scattering $N\sigma_s$	Capture $N\sigma_c$			
H	1	0.85	0.013	1	0.85	65
D	2	0.10	0.0000015	0.72	0.072	47,500
He	4	0.029	0	0.425	0.0123	∞
Li	7	0.092	2.9	0.26	0.024	0.0083
Be	9	0.73	0.0011	0.2	0.146	133
B	11	0.42	97	0.17	0.071	0.00073
C	12	0.39	0.00036	0.15	0.058	162
N	14	0.35	0.061	0.13	0.045	0.74
O	16	0.18	0.000068	0.12	0.0215	316
F	19	0.14	0.0023	0.10	0.014	6.1
Ne	20	0.067		0.095	0.0064	
Na	23	0.085	0.012	0.083	0.0071	0.59
Mg	24	0.14	0.016	0.080	0.0112	0.70
Al	27	0.080	0.012	0.070	0.0056	0.47
Si	28	0.088	0.013	0.070	0.0062	0.42
P	31	0.34	0.01	0.06	0.0204	2.04
S	32	0.051	0.018	0.06	0.00306	0.17
Cl	35.5	0.26	0.87	0.055	0.0143	0.0165
A	40	0.040	0.013	0.050	0.0020	0.154
K	39	0.019	0.028	0.050	0.00095	0.034
Ca	40	0.22	0.01	0.050	0.011	1.1

NOTE:
N = number of nuclei per sq cm = number of atoms per sq cm.
§ = fractional energy loss of neutron per collision with a nucleus.

TABLE 128. SOME HIGH-MELTING-POINT COMPOUNDS OF HIGH-MODERATING-RATIO ELEMENTS
For Thermal Neutrons

Material	Formula	Melting point, °C
Beryllium oxide	BeO	2520
Beryllium carbide	Be_2C	2100 decomposes
Carbon	C	3500

comparison of the light elements as moderators. Table 128 lists a few of the high-melting-point compounds of elements possessing light nuclei.

6. Summary and Conclusions. The Atomic Energy Commission[5] has recently stated

> . . . practical uses of atomic power will not be developed for at least ten years and it will be still another ten years before the influence of atomic energy is felt in the world. This does not mean that by September, 1949 electric power could not be actually developed by atomic energy. But what is definitely not near at hand are large-scale, commercial applications of power from atomic energy.
>
> Materials used in an atomic power plant must be able to stand high temperatures. These construction materials must have another special property—they must not be too prone to consume neutrons. Proper coolants must be perfected. Methods must be perfected for removing radioactive by-products from the piles. Other problems are the development of quick-acting "throttles" (control rods) and methods of shielding the workers against radiation.
>
> Still another problem is to have adequate stocks of uranium or plutonium to activate a sizable atomic power industry. The A.E.C. has undertaken research to try to "breed" new nuclear fuel in the very process of consuming the original fuel. A breeder is a nuclear chain reactor which over a period of time will actually create more fissionable material than is put into the reactor as fuel to sustain the reaction. If this regeneration of nuclear fuels can fully replace the original materials then all of the natural uranium and the world's supply of thorium, which is more plentiful than uranium, constitute potential nuclear fuels.

In summation, it may be said that the great interest in nuclear power is based on the following attractive features.

1. The small weight of fuel for a given power release
2. No need for gaseous oxygen, permitting use in the stratosphere
3. Possibility of a large amount of power per unit weight

The eventual use of large-scale nuclear power plants is dependent upon developments in many scientific fields. The future developments in refractory research, development, and production will undoubtedly play an important role in this realization.

CHAPTER XXV

REFRACTORIES FOR GAS-TURBINE AND JET-PROPULSION ENGINES

1. Introduction. Since the previous edition of this book, great strides have been made in the development of gas-turbine and jet-propulsion devices for airplanes and guided missiles. During the Second World War the Germans were particularly active in this field, producing turbo-jet fighter planes of high performances and, later, liquid-rocket-propelled planes of high speed but very short flight times. They also produced the V-1 and the V-2 guided missiles, which would have been extremely destructive to the Allies if the war had lasted longer. All these developments were based on sound fundamental research carried out in a large number of high-speed wind tunnels; and therefore, in this field they were ahead of other nations. At the same time, an interesting development of the turbo-jet engine was carried through in England by Colonel Whittle, which in many ways was superior to the contemporary German engines. During the latter part of the war and since that time, we have been very active in this country in fundamental research and applications of jet propulsion devices and have made great advances in increasing the performance of these engines. In fact, it is generally believed that no high-speed aircraft of the future will use the reciprocating engine.

It is extremely difficult to say just how far refractories will enter into the future picture of this development. At present, very little refractory is used in any of these engines, but the desire for higher temperatures, less complicated cooling devices, and less use of strategic materials has developed a great interest in refractories, and much research is now being carried out in this particular field. The problem of satisfactorily adapting the refractory is a most difficult one because of the high temperatures, high rate of temperature change, and high gas velocity; but as the amount of refractory used would be comparatively small, the cost per pound enters into the picture only to a small degree, and this has stimulated research to extend out into fields of refractories that have not previously been explored. It is hoped in this section to give a very brief picture of the jet-propulsion engine and its operating conditions, together with the possibilities of improving its performance by the use of the proper refractory.

2. Types of Power Plants. *Gas Turbines.* The gas turbine to supply power for marine propulsion or locomotive use is quite similar to the well-known steam turbine except that the steam is replaced by combustion gases. In Fig. 372*A* is shown a diagram of such a turbine. *a* is a compressor that draws in air from the atmosphere and forces it into the combustion chamber *b*, where it is mixed with atomized fuel and the mixture burned to produce a temperature of 1200 to 1500°F (about 650 to 800°C) where it enters the turbine *c*. The power derived from the turbine is carried through the shaft *d* to drive the compressor, and useful power is taken from the shaft extension *e*. It should be realized that the actual power produced by the gas turbine is several times the amount of useful power output because of the large proportion of the turbine power taken by the compressor. In spite of this, the unit is relatively compact and light compared with a unit of similar power using either a diesel engine or a steam generator and turbine. With a compression ratio of 20, if such a figure can be attained in practice, a turbine without regeneration would have a maximum efficiency[10] of 25 per cent at 1500°F (about 820°C) turbine entrance temperature and 36 per cent at 3000°F (about 1650°C). If regeneration is used with a compression ratio of 4, these efficiencies are increased to 39 and 50 per cent, respectively. Thus, it is seen that refractories would be highly desirable for a combustion chamber and turbine parts if they could be developed with high creep values, temperature shock resistance, and fatigue resistance. In general, the atmospheric conditions in the combustion chamber and turbines are oxidizing, but there would certainly be times when at least portions of the structure would have reducing gases in contact with them. A relatively long life, perhaps 10,000 hr, is desirable for the refractories in this application.

Propeller-turbo-jet. For aircraft and guided-missile propulsion, several novel power plants are now in use. The most conventional is the so-called propeller-turbo-engine as shown in Fig. 372*B*. The propeller *a* is driven by the gas turbine *b*, which is also connected to the axial compressor *c* in the same way as in the previous example. Because of the high velocity of the airplane, air is forced into the diffuser *d*, built up to higher pressures by the compressor, and forced into the combustion chamber *e*, where fuel is added and burned. From here it goes through the nozzle blades *f* into the turbine and then out through the tail pipe *g*. Thrust is provided both by the power supplied to the propeller and by the inertia of the gases leaving the tail pipe. In this case, with a combustion ratio of 4, efficiencies[10] of 24 per cent are possible with 1500°F (about 820°C) turbine-entrance temperature and 30 per cent at 3000°F (about 1650°C), again showing the value of high-temperature materials.

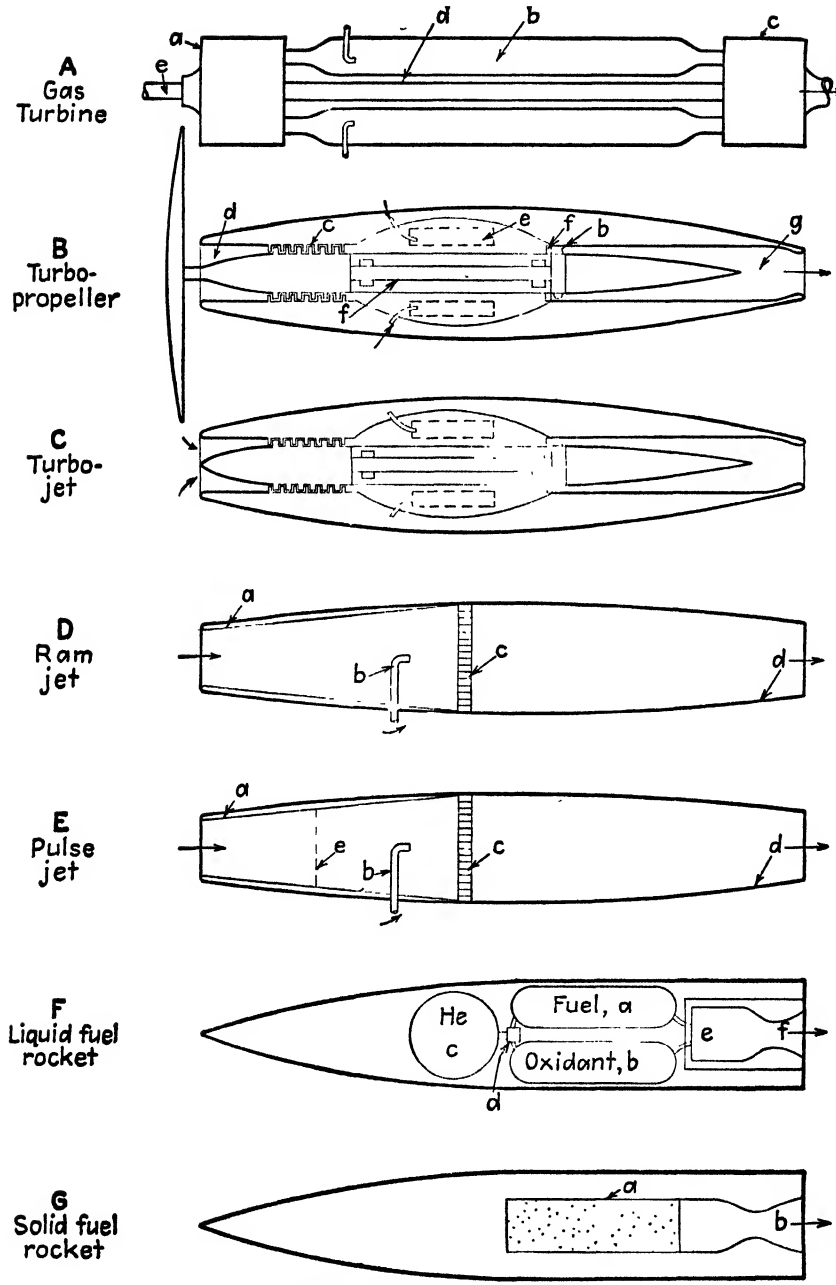


FIG. 372. Jet-propulsion engines.

Turbo-jet. The turbo-jet engine shown in *C* of Fig. 372 is the same as the previous example except that the propeller is omitted and the thrust comes entirely from the velocity of the gases passing out of the tail pipe. The effective power P delivered by such an engine is given by the following:[12]

$$P = \frac{W}{g}(V_1 - V_2)V_2$$

where W = the weight of gas, lb/sec, from tail pipe
g = the acceleration of gravity
V_1 = the discharge velocity of the gas, ft/sec
V_2 = the velocity of the aircraft, ft/sec

The propulsive efficiency η is given by

$$\eta = \frac{\text{output}}{\text{input}} = \frac{(W/g)\ (V_1 - V_2)V_2}{(W/g)\ (V_1^2 - V_2^2)}$$

The maximum output occurs when $V_1 = 2V_2$, and here η = has a theoretical efficiency of 66.7 per cent.

This type of engine is relatively efficient compared with the reciprocating engine only at the higher speeds but has greater simplicity, low weight per horsepower, and, most important for high speeds, a small frontal area per horsepower. At speeds of 400 to 600 mph, the fuel consumption is now somewhat greater than for an equivalent reciprocating engine. The temperature now reached in production engines is somewhat as shown in Table 129.

TABLE 129. TEMPERATURE IN TURBO-JET ENGINES

Part	Temperature	
	°F	°C
Combustion chamber wall (metal)	400–1200	200–650
Gas exit from combustion chamber	1500–2000	820–1100
Turbine nozzle blades	1000–1800	540–980
Turbine buckets	1000–1500	540–820
Tail pipe	500–1000	260–540
Tail pipe gas temperature	800–1500	430–820

In contradiction to other engines, this type does not show increased efficiencies[10] with temperature above those generally used; *e.g.*, at 1500°F (about 820°C) it is only 12 per cent. However, it should be remembered that with this engine as well as the other types, higher temperature means increased thrust horsepower, so that even in this case higher temperatures

would be desirable for short periods of high output, even at the expense of greater fuel consumption.

Ram-jet. A quite different type of engine is the ram-jet shown in *D* of Fig. 372. This engine is of the most simple construction, as there are no moving parts and the structure is light. However, its efficiency is high only at supersonic speeds, and it has the disadvantage of not being self-starting, as it must be propelled up to a speed of somewhere around 400 mph before it will begin to deliver effective thrust. Air enters the diffuser *a* at the velocity of the engine and is compressed to a higher pressure at *b*, where fuel is injected and burned. A grid at *c* stabilizes the flame, and the hot gases are then forced out through the tail pipe *d* at a very high velocity, thus producing the effective thrust. With an exhaust temperature of 1500°F (about 820°C) an efficiency[10] of 29 per cent is reached at 2,000 mph, while at 3000°F (about 1650°C) the efficiency reaches 40 per cent at somewhat over 3,000 mph. The pressure in the combustion chamber would run to 500 psi at 1,800 mph. The temperatures in the combustion chamber may run to 3000°F (about 1650°C), and the exit velocity from the tail pipe up to twice the air speed. In the latter part of 1947, it was announced that two models of ram-jet-driven missiles had exceeded 1,400 mph, or twice the speed of sound.

Pulse-jet. The pulse-jet as shown in Fig. 372*E* is similar to the preceding example except that a valve *e* permits the pressure in the combustion chamber to build up at each explosive cycle and force the hot gases through the tail pipe *d*. The pressure then drops in the combustion chamber below the dynamic pressure in the diffuser, which opens the valve *e*, fills the combustion chamber with fresh air, and the cycle is then repeated. This engine was used by the Germans on their V-1 guided missile at speeds of 400 to 500 mph. The efficiency at these speeds is not very high, but this is not important for short flights, and the simplicity of producing such a device compared with a reciprocating engine of the same power makes its use for expendable missiles quite advantageous. The atmosphere in the combustion chamber of both the ram-jet and the pulse-jet are close to neutral, but this does not mean that oxidation or reducing conditions are not occasionally obtained at various points of the structure.

Liquid-fuel Rocket. A brief history of the liquid-fuel rocket is given by Wyld.[16] A motor of this type is shown in Fig. 372*F*. Unlike the previous engines, no air is required for combustion, so that the motor is adapted for flights at extremely high altitudes in the stratosphere. The fuel *a* and the oxidant *b* are carried in separate tanks. When the rocket is started, pressure from the helium reservoir *c* passes through the reducing and control valve *d* to force the fuel into the combustion chamber *e*, where it is immediately burned, and the exhaust gases pass out through the nozzle *f*. A rocket

motor is very light and may deliver as much as 100 thrust horsepower per pound of weight. The German V-2 rocket used liquid fuel and had the following characteristics:

TABLE 130. CHARACTERISTICS OF THE GERMAN V-2 ROCKET

Weight at start	20,000 lb
Maximum thrust	60,000 lb
Combustion chamber pressure	225 psi
Flame temperature	5000°F (about 2760°C)
Nozzle velocity	8,000 ft per sec
Time of combustion	200 sec

A number of airplanes such as the German Me-163B and the Bell XS-1 have been flown with liquid-fuel-rocket engines. For control purposes several combustion chambers are used, as it is difficult to throttle down a single nozzle. The total time of combustion seldom exceeds 3 min. The extremely high temperatures produced in the combustion chamber and nozzles have made cooling of the walls necessary, which is generally done by recirculating some of the fuel around the wall before it enters the combustion chamber. Also fuel is sometimes injected through the wall itself to provide a film on the inner side, which gives evaporation cooling. Refractories have also been used in the nozzle section, but little information is available concerning them. Combustion conditions are usually reducing, and chamber pressures now do not exceed 300 psi, but higher pressure should be expected in the future. A few of the fuels suggested for use in rockets of this type are listed in Table 131.[12,15]

TABLE 131. PROPERTIES OF SOME FUEL COMBINATIONS

Fuel	Oxidant	Calculated combustion temperature		Exhaust velocity at sea level ft per sec
		°F	°C	
Nitromethane (monopropellant)		3950	2180	6,150
Aniline	Red fuming nitric acid	5070	2800	6,200
Methyl alcohol	Hydrogen peroxide (76 per cent)	4160	2290	6,300
Liquid hydrogen	Liquid oxygen	4390	2420	10,150
Ethyl alcohol	Liquid oxygen	5260	2910	6,870

Solid-fuel Rockets. The solid-fuel rocket is well known and is shown in *G* of Fig. 372. Here the fuel *a* burns in a metal combustion chamber and

passes at a high velocity through the nozzle *b*. Combustion chamber liners and nozzles of refractory would be valuable here, and much research is now being carried out on this development. The temperatures, pressures, and velocities are high but of short duration. These rockets are used as missiles such as the "bazooka" for antitank weapons and the "Jato" for assisting airplane take-offs. Chamber pressures of 500 to 4,000 psi are encountered with exit velocities up to 6,000 ft per sec. The duration, however, is seldom over 15 sec.

3. Combustion Chambers. *Turbo-jets.* In this engine the temperature in the combustion chamber is not particularly high, perhaps 2000°F (about 1090°C) at the most, and the pressure seldom exceeds 100 psi. However, the heat shock is severe in periods when the engine is started and stopped, and there is some erosion, which tends to carry any loosened particles into the turbine. In the conventional type of combustion chamber

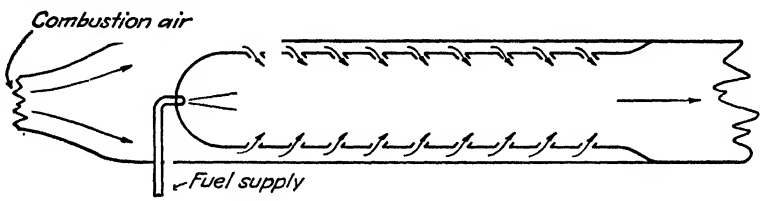


FIG. 373. Turbo-jet combustion chamber.

made of metal, as shown in Fig. 373, the cooling takes place by the surrounding air and infiltration of this air through holes in the walls of the combustion chamber. Up to the present time, the work on refractories has been mainly to attempt to produce a replica of the metal in a refractory material by the usual ceramic methods, but it would seem evident that a complete redesign to take advantage of the refractories will be necessary before a satisfactory solution is arrived at. Coatings have also been tried as a means to reduce scaling and to reduce heat flow through the combustion tube walls.

Ram-jets. As far as it is known, no refractory linings have been used in ram-jets, but a lining to permit higher flame temperatures would certainly be an advantage. Since the pressures may run up to 500 psi, the refractory would have to be rigidly supported, as breathing of the wall tends to crack the lining. The heat-shock resistance of the lining must also be good because the temperature builds up very rapidly at the start and would also drop rapidly immediately after the fuel is shut off. Coatings on the inside of the combustion chamber, however, have been tried.

There would be some advantage in producing a flame holder from refractory materials if it could be constructed to stand the heat shock and erosion of the rapidly moving gases.

Rockets. The heat release in the rocket is tremendous, amounting to as much as 20 million Btu per cu ft per min. At present it is necessary to cool the rocket walls by using the fuel regeneratively, and this works out satisfactorily only in the larger rockets because the amount of fuel is insufficient in the smaller sizes. A good refractory liner, even though thin, would materially reduce the amount of heat transferred to the fuel and might eliminate cooling entirely. However it would not, as some believe, appreciably increase the thermal efficiency, for only a very small proportion of the total heat passes through the most highly conducting wall. Here again the refractory would have to be well supported if pressures up to 300 psi were encountered, together with the severe temperature shock. Construction of the chamber lining would be a single cylinder in the smaller sizes as shown in Fig. 374*A*, or it might be made up in the larger sizes with

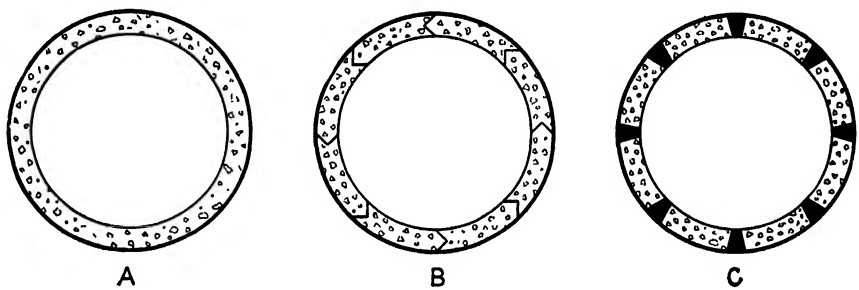


FIG. 374. Cross sections of refractory combustion-chamber liners.

a series of interlocking staves as shown in Fig. 374*B* with a rigid metal casing. These staves will permit a certain flexibility of the structure and give better heat-shock resistance. Another suggested method is a thin plastic refractory lining supported by pins welded to the inside of the combustion chamber much as the Bailey stud wall is used in steam boiler furnaces, as in Fig. 374*C*. This construction would seem to have considerable promise if its resistance to erosion could be made sufficiently great. Still another suggested method is to use a coating on the inside of the combustion chamber of a high-temperature enamel or refractory paint. Such an enamel as developed by the Bureau of Standards[14] has proved quite interesting in tests, as it reduces corrosion and permits less heat flow into the metal. More recent work at the University of Illinois has produced some interesting coatings for metal and graphite.[17,18]

4. Nozzles. *Liquid Rockets.* In this type of rocket, the nozzle is almost always cooled by regenerative circulation of the fuel, and then the heat flow through the wall amounts to as much as 2½ to 4 Btu per sq in. per sec. The use of regenerative cooling at the higher temperatures means a considerable pumping loss; and as stated before, in the smaller units there

is not enough fuel to give a satisfactory amount of cooling. This regenerative cooling has been supplemented by film cooling, where a small amount of fuel passes through the wall in small holes and flows over the inner surface and by so-called sweat cooling where the fuel permeates the wall and cools by evaporation on the inner surface. An adequate refractory for the nozzle section would certainly lessen the necessity for cooling at higher temperatures, but it must be extremely resistant to erosion and heat shock. It would seem necessary, also, to have the inside of the nozzle smooth to reduce mechanical losses.

Solid-fuel Rocket. In this case, conditions at the nozzle are quite similar to that of the liquid-fuel rocket, but the duration is generally less; and as regenerative cooling is impossible, refractories are more generally used. The material must have high-temperature shock resistance and be able to withstand erosion under the very high velocity. While loosening of the particles from the refractory is not so serious in the rocket as in the turbo-jet where serious trouble may result in the turbine, it is found that when erosion loosens small pieces, they act as sand in a sandblast and wear out portions to the rear. Some of the material suggested for nozzles are

Graphite with silicon carbide coating
Silicon carbide
Graphite and silicon carbide mixture
Fused alumina and silicon carbide
Graphite and metal mixtures
Plaster of Paris and graphite mixtures
High-temperature porcelains

5. Guide Vanes and Reactors. A rocket, such as the V-2, is guided by small vanes extending into the stream of gases from the nozzle. These vanes must withstand temperatures up to 5000°F (about 2750°C), but only for short periods. Dense graphite has been used for this purpose quite satisfactorily.

6. Turbine Buckets. Many attempts have been made to replace the metal buckets in the turbine with refractory materials. The earliest work was carried out by the Germans during the Second World War, perhaps not so much at that time to find materials superior to the metals, but to find materials as substitutes for the high-temperature alloys, which were very scarce in that country. A great deal of effort in this country was directed toward the production of metals of very high creep resistance, and a really amazing improvement was reached in creep strength for alloys containing Co, W, and Mo. However, these metals are not plentiful, and it would be difficult to find sufficient quantities in an emergency.

It might be interesting to try to make a comparison between metals and ceramic materials at the temperature of the gas turbine. Although we have

excellent creep data on the high-temperature alloys, the data on refractories are very meager indeed, and a great deal of work needs to be done in this field. However, in Fig. 375 are shown comparative creep values for several metals and refractories, indicating at least a possibility of producing high-creep-strength ceramic materials for the higher temperature ranges. It should be remembered that the density of the ceramic materials is roughly one-half that of metals, and therefore the stresses reached in the turbine blades will be that much less, giving the ceramic materials some advantage. In Fig. 376 is shown the hot breaking strength of some oxides and a high-temperature alloy. While the high breaking strength does not have so much significance as the creep values, it does indicate a possibility of producing strength in oxides greater than those in alloys, and at any rate we must realize that the oxidation of our best alloys is so great above 1800°F (about 980°C) that they would be useless except for very short periods of heating.

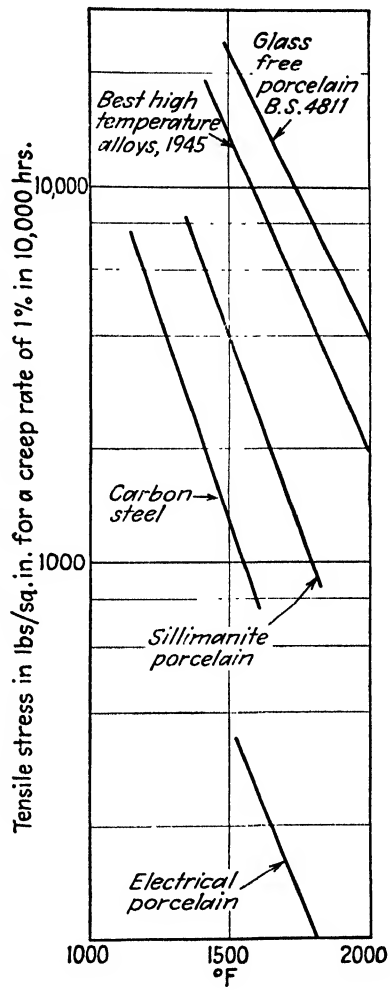


FIG. 375. Comparative creep values for metals and ceramics.

Some of the more promising refractories for buckets have been discussed in Chap. XII, such as glass-free porcelains developed by the Bureau of Standards from a beryllium oxide or zirconia base. In Germany, some research was carried out on fused quartz buckets, but they did not seem to have enough advantage in temperature limit over metals to make them particularly interesting. Also metal-bonded oxides[8] and metal-bonded carbides have been suggested and tested with the idea of increasing the temperature-shock resistance, but little is known of their creep values. One German turbine had the buckets mounted on the inside of a rotating shell so that they would always be in compression.[5]

Also, some work has been done on the coating of metal buckets with a refractory enamel, mainly to reduce the oxidation.[14,17,18] This step would certainly not appreciably raise the creep limit; however, for low-stressed parts and short time intervals, it would seem as if these coatings would permit replacement of alloys with carbon steel.

As most of the turbine buckets made from refractory materials must be very carefully dimensioned, it has been necessary in most cases to size them

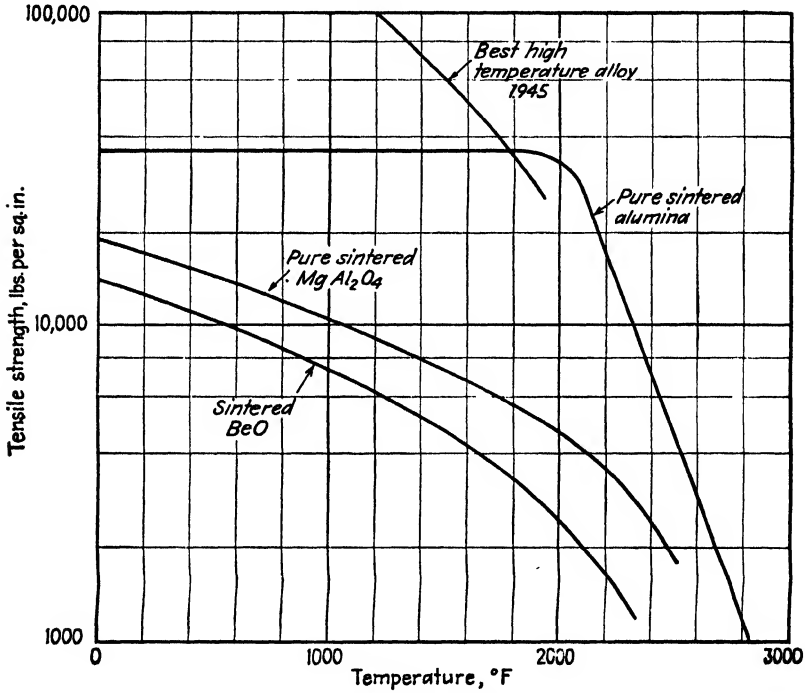


FIG. 376. Comparative hot tensile strengths for metals and ceramics.

with diamond wheels after firing, but this is a very costly operation. Then it would seem difficult to produce as thin a trailing edge on the bucket of a refractory as it is possible to obtain with metal, and therefore the over-all efficiency of the turbine is somewhat decreased when using the refractory. Also, it should be remembered that the refractory bucket at room temperature is brittle and handling difficulties will be experienced.

Another serious problem is the fastening of the ceramic bucket into the rotor. One method[5] tried in Germany was to ram iron powder between the blade and the socket and then sinter it. Another method[8] consisted in silvering the base of the blade and then heavily plating with copper, so that on clamping a yielding layer would distribute the stresses.

In regard to the future, it will certainly be necessary to carry on more fundamental work on glass-free oxide bodies with a minimum of impurity. These will have to be tested for creep rate, fatigue, impact, and heat-shock resistance. Also, the carbides, borides, and nitrides are quite promising, and work on these should be carried out simultaneously. Basic research should be stressed for the next few years to form a sound foundation on which to build future specific research.

7. Turbine Nozzle Blades. These blades have to encounter the same conditions as the turbine buckets, but the stresses are much lower and materials having higher creep rates could be used. On the other hand, if a material is satisfactorily developed for a turbine bucket, it would also be satisfactory for the nozzle blade.

8. Turbine Rotors. The turbine rotor has been experimentally produced in refractory materials, but the problems of attaching blades have not been entirely solved. At any rate, there is not such a great advantage in using refractories for this part, as the metal rotor can be cooled without too great a loss in the turbine efficiency.

9. Insulation. Portions of the jet engines must be insulated to prevent the interior of the airplane from becoming too hot. The long tail pipes in some of the jet fighters run down the fuselage and present considerable area. The insulation should be light, efficient, and stable under temperatures up to 1800°F (about 980°C) and severe mechanical vibration. Probably no thermal insulation is now available that exactly fits these specifications.

10. External Portions of the Rocket. When a rocket, after a high-altitude flight, returns to the earth's atmosphere at a speed of several thousand miles per hour, the surface of the war head and projecting vanes will heat by friction to 1200°F (about 650°C) or higher. To limit the rate of penetration of this heat to the explosive charge, an insulating coating on the metal would be very desirable.

11. Summary. It is still not clear how useful refractories will become in future jet-propulsion devices. However, the possibilities of increased performance by the use of refractories is so great that we should bend all efforts to develop them for this purpose. To this end a far larger proportion of research than at present should be directed toward fundamental studies such as the mechanism of sintering, long-time creep tests, high-temperature fatigue tests, and damping tests, as well as resistance to gas attack and thermal shock. Then again, we should not forget the fact that the materials going into the high-temperature alloys are rather limited, which may well mean that large-quantity production of engines using them will be impossible in a future emergency. The development of good coatings may permit the substitution of carbon steel for the high-priced alloys where the stresses are not high, as in tail pipes, but only high-grade refrac-

CHAPTER XXVI

USE OF REFRACTORIES IN MISCELLANEOUS INDUSTRIES

1. Kilns. *Periodic Kilns.* The periodic kiln is used in the ceramic industry mainly for the firing of refractories and heavy clay products, with the use of coal as the principal fuel, although natural gas and oil are also used. A typical example of a round downdraft kiln of this type is shown in Fig. 134 of Chap. IX. The maximum temperatures obtained in these kilns run from 1800°F (about 980°C) for some building brick to 2800°F (about 1540°C) for silica brick.

The refractories used in the kiln are always fireclay brick, using low- or intermediate-duty brick for heavy-clay-products kilns and high-heat-duty or super-duty brick for the higher temperature kilns. Because of the fact that the kilns are heated and cooled fairly rapidly, silica brick would not be satisfactory.

Recently, a number of periodic kilns have been constructed with a lining of insulating firebrick. They have shown distinct advantages over those lined with heavy types of brick. Kilns of this type have been used for firing common brick and also for firing glass-tank blocks with temperatures of 2600 to 2700°F (1430 to 1480°C). The main advantage in using the insulating firebrick is the great reduction in the heat stored in the walls and crown of the kiln. In many cases, this heat storage has been cut down to 25 per cent of the value for heavy bricks. This means, of course, a substantial saving in the fuel required for heating the kiln, a quicker turnover so that a kiln can produce more ware, and, perhaps as important, a more even temperature distribution over the kiln itself.

The refractories in periodic kilns generally have a comparatively long life, many kilns in operation having had only minor repairs in the last 15 or 20 years. The main source of trouble is spalling of the crown brick over the fireboxes, shrinking and softening of the bag walls, and slagging from the coal ash around the furnaces. With the use of forced draft and forced cooling of the kilns, the spalling tendencies are increased but, even under these conditions, are not particularly severe. The use of insulating firebrick has not been studied for a sufficiently long period to give accurate information on the life; but from indications that we already have, it would seem that the life would compare favorably with the heavy brick.

The use of outer insulation on periodic kilns is increasing, especially on the crown. Although it is difficult to give any exact figures on fuel saving, the insulation does show a definite increase in economy and also enables a more uniform temperature to be maintained in the kiln. Of course, it may be necessary, when insulation is used on a high-temperature kiln, to employ a better grade of refractory to withstand the load at the higher mean temperature reached by the lining.

Continuous Kilns. The tunnel kiln has been described in Chap. IX. In general, the requirement for this type of kiln is a refractory lining that will give long, uninterrupted service at the required temperature level. There is little or no tendency to spall because the temperature at any one place is constant. Usually the wall bricks must have good strength and abrasion resistance in case ware rubs against them during an accident. Therefore, in the modern kiln construction, low-heat-duty fireclay brick is used in the heating and cooling zones and intermediate- or high-heat-duty brick in the hot zones, although for some types of kiln running at high temperatures, super-duty fireclay or kaolin bricks are found useful.

The tunnel kiln, of course, must be very thoroughly insulated throughout its length; otherwise, a large amount of heat would be lost from the great amount of surface exposed. This is accomplished with insulating brick or blocks on the sides and a loose insulation on the top.

Some tunnel kilns have been constructed with a lining of insulating firebrick; but in this case, a low heat storage is not so important as with the periodic kiln and therefore the insulating firebrick does not have so great an advantage. However, from one point of view, this type of construction shows real economy, *i.e.*, in the kiln that must make a change in temperature to accommodate various types of ware fired. It is found that with the kiln lined with the insulating firebrick, a change in schedule can be made in a few hours with a minimum loss in ware during the turnover whereas with a heavy brick kiln, this change of schedule may take a day or more and the loss in unproductive firing is much greater. Also, the lighter weight construction can use lighter steelwork and foundations.

Some tunnel kilns are indirect fired and have a muffle lining. This muffle should, of course, have a high thermal conductivity, good hot strength, and stability over long periods of time. Such muffles are usually made of clay-bonded silicon carbide or clay-bonded fused alumina. There are, however, certain temperature ranges in which the silicon carbide tends to oxidize, and care should be taken to follow the recommendations of the manufacturer of the refractory in its use.

Perhaps the portions of the kiln giving the most trouble are the car bottoms, because they are alternately heated and cooled each time that they pass through the kiln and, for this reason, suffer from thermal shock.

There also is the difficulty that setting sand used in kilns firing refractories or heavy clay products will fall into the cracks between the car blocks when they are cool; then as the car heats, the blocks are forced apart and there is a gradual growth in the size of the car top until it eventually rubs on the kiln. For this reason, car bottoms are usually made of large shapes, and some manufacturers blow out the sand from the bottom of the car with compressed air each time that it comes out of the kiln. Considerable success has been had lately with car tops made of a lightweight castable mix, which can be put on the car very cheaply by unskilled labor, a construction that seems to give good life in many installations.

Kiln Furniture. In the last few years, a great deal of study has been made of the question of saggers, not only to increase their average life but also to reduce their wall thickness and weight for a higher efficiency. Many potteries are now purchasing saggers from refractory manufacturers rather than attempting to make their own. The old method of putting green saggers on top of the bungs filled with ware for the first firing has been largely superseded by prefiring the saggers at a somewhat higher temperature than would be used, with a consequent increase in strength. Although thirty years ago the average life of the sagger was only 15 burns in a kiln, a life of twice that is now obtained, and instances of even greater life are often found. The recently developed loose-bottom sagger does much to reduce the heating and cooling stresses.

In manufacturing the sagger, care is taken in sizing the grog to a definite screen analysis and a more uniform structure is obtained in forming, often by the casting method. Although most of the saggers are still made of fireclay, special talc bodies have been tried as well as bodies containing alumina and silicon carbide. For glost work, the question of dusting is a very important one and must be considered along with the other characteristics of the body used.

The open setting of ware has been making great strides in almost all types of whiteware firing. Electrical porcelains, sanitary ware, and semivitreous table ware are now fired in open settings with a considerable increase in kiln capacity and a lower fuel cost per unit ware. The open-setting method consists in supporting a series of slabs on corner posts until the car is built up to the required height, as shown in Fig. 314, Chap. XIX. Attempts are made, of course, to keep the thickness of the slab to a minimum and give the whole structure the greatest possible life. The furniture is usually made of clay-bonded silicon carbide, although clay-bonded fused alumina and zircon refractories have been used. Many ingenious methods have been developed for supporting the slabs to minimize expansion stresses and still give a stable structure. There is still some difficulty with the slabs made of silicon carbide, in that they tend to increase in size, or grow,

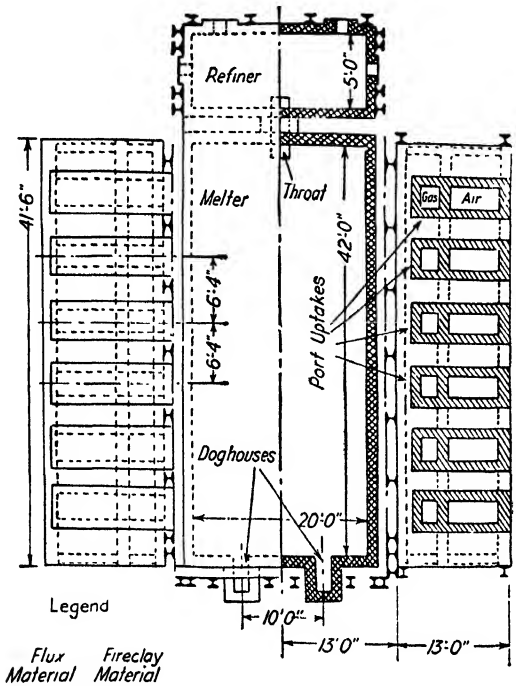
owing to gradual oxidation, each time that they go through the kiln. However, some of the more modern types of refractory have minimized this difficulty by surface coatings or other means to protect the silicon carbide from the air.

2. Glass Refractories. *General Types of Melting Furnace.* Glass is melted in a number of types of furnace, one of them being the pot furnace where the glass is melted in open or closed pots, similar to a crucible, with the heat applied to the outside. This type of melting would be used for small batches of glass or glass necessitating very careful control, such as colored or optical glass. For larger production, small reverberatory furnaces called "day tanks" are used, where the glass is melted in a hearth usually by producer gas using regenerators. The batch is melted down and worked out usually in a 24-hr period, a new batch put in, and the process continued. For larger quantities of glass, the continuous tank is universally used, where raw materials are fed in at a steady rate at one end and the glass drawn off continuously at the other end. These continuous tanks may be classified as bottle tanks for making containers and sheet-glass tanks for making window and plate glass by the continuous process.

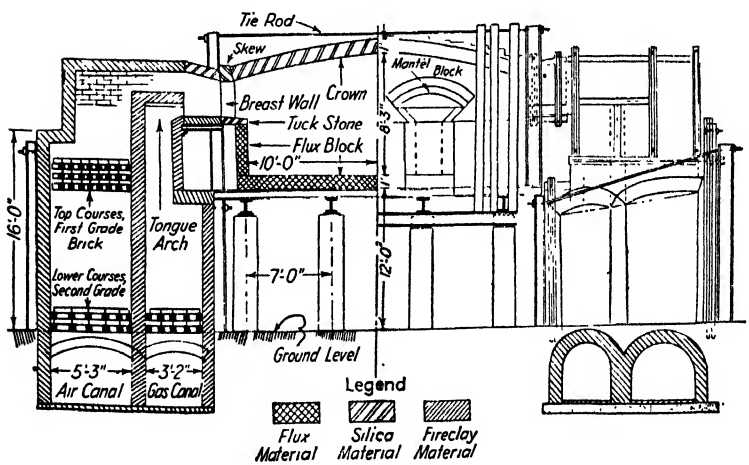
Recently platinum crucibles of considerable size have been used for melting optical glass. Here there is no solution of refractory in the glass, and consequently a more transparent and homogeneous product results. It is understood that a small tank has been made from platinum by one of our large glass manufacturers.

A Typical Tank for Bottle Glass. It will, perhaps, be best to take as an example of a continuous tank for making bottle glass the furnace shown in Fig. 377. This furnace consists of a melting chamber fired by producer gas preheated by a series of regenerators and a refining section connected to the melting section by a throat below the surface of the glass. This refining section receives no direct heat but is kept hot by conduction and radiation from the melting section. The temperature in the melting section is around 2600 to 2800°F (about 1430 to 1540°C); whereas in the refining section, it is reduced to perhaps 2300°F (about 1260°C). From the refining section, the glass is drawn out into forehearths that have separate burners to maintain a uniform temperature.

The glass tank below the surface of the glass is composed of flux blocks that are generally a dense fireclay-grog-ganister mixture in comparatively large units in order to reduce the number of joints. A common size of these blocks would be 12 × 24 × 42 in., and they are usually ground accurately to size so that the joints are as thin as possible. No insulation is used around the bottom of the tank, as the higher mean temperature permits more rapid solution of the blocks in the glass and also tends to



(a)



(b)

FIG. 377. (*a*) Plan view of producer-fired regenerative-type glass furnace. (*b*) Half section on center line of first port, producer-fired regenerative-type glass furnace. (*Courtesy of Owens-Illinois Glass Co., Toledo, Ohio, from "Manual of ASTM Standard on Refractory Materials."*)

TABLE 132. CLASSIFICATION OF REFRACTORIES FOR GLASS FURNACE
(From "Manual of ASTM Standards on Refractory Materials")

Furnace part	Material	Temperature	Slagging action	Corrosion erosion	Abrasion	Spalling	Remarks
Melter: Bottom, Side, Ends	Highly siliceous hand-made, machine-made, or slip-cast block; Molten cast block of high-alumina content	2500 to 2900°F. (1370 to 1595°C.)	Severe	Severe	Moderate	Slight	Spalling is of importance only during heating
Refiner: Bottom, Side, Ends	Same as melter	2350°F. (1290°C.)	Moderate	Moderate	Moderate	None	Same as melter
Tank crown	Silica brick	Up to 2900°F. (1595°C.)		Moderate	Severe in some furnaces	Important	
End walls	Silica brick	Up to 2900°F. (1595°C)	Moderate	Severe in some furnaces	Severe in some furnaces		
Breast walls	Silica brick High-alumina brick	Up to 2900°F. (1595°C.)	Severe	Severe	Severe		
Port jambs	Silica brick High-alumina brick	Up to 2900°F. (1595°C.)	Severe	Severe	Severe		
Port sills	Silica-block High-alumina block	Up to 2900°F. (1595°C.)	Severe	Severe	Severe		
Port wall sides	Silica brick Fireclay brick	Up to 2900°F. (1595°C.)	Severe	Severe	Severe		
Port crowns	Silica brick Fireclay brick	Up to 2700°F. (1480°C.)	Moderate	Moderate	Severe in some furnaces		
Port paving	Silica brick Fireclay brick	Up to 2700°F. (1480°C.)	Severe	Severe	Severe in some furnaces		
Tongue arches	Silica brick	Up to 2900°F. (1595°C.)	Moderate		Severe in some furnaces	Important	Spalling very important during heating

TABLE 132. CLASSIFICATION OF REFRACTORIES FOR GLASS FURNACE (*Continued*)

Furnace part	Material	Temperature	Slagging action	Corrosion erosion	Abrasion	Spalling	Remarks
Mantle block	Fireclay block High-alumina block	2500°F. (1370°C.)		Severe	Moderate	Important	
Regenerator wall crown	Fireclay brick	Up to 2000°F. (1090°C.)	Moderate	Moderate	Severe in some furnaces		
Checkers	Fireclay brick High-alumina brick	Up to 2000°F. (1090°C.)	Severe	Severe	Severe	Very important	Silica and magnesite are sometimes used
Shadow wall	Silica brick	Up to 2800°F. (1540°C.)					
Tuckstones	Silica block Fireclay block High-alumina block	Up to 2900°F. (1595°C.)	Severe	Severe	Severe		
Throat	Same as tank block	2600°F. (1425°C.)	Severe	Severe			
Invert arches	Silica shapes	Up to 2900°F. (1595°C.)	Severe	Severe	Severe	Important	
Bridgewall covers	Fireclay block	Up to 2800°F. (1540°C.)					
Burner-block	Silica Fireclay High alumina	Up to 2700°F. (1480°C.)	Severe	Severe	Severe	Important	
Skimmers	Siliceous fireclay block High-alumina block	Up to 2600°F. (1425°C.)	Moderate	Moderate		Important	
Feeder-tubes	Siliceous fireclay High alumina	Up to 2600°F. (1425°C.)	Moderate	Moderate			
Troughs	Fireclay High alumina	Up to 2400°F. (1315°C.)	Severe	Severe		Important	Must have good transverse strength
Plugs	Fireclay High alumina	Up to 2400°F. (1315°C.)	Severe	Severe		Important	Must have good tensile strength
Revolving tubes	High alumina Fireclay Siliceous special material	Up to 2300°F. (1260°C.)	Moderate	Moderate	Severe	Important	Must have good shear strength
Plunger needles	Same as tubes	Up to 2300°F. (1260°C.)	Moderate	Moderate		Important	Must have good tensile strength

float the blocks out of the bottom. In fact, air cooling is regularly used on the outside of the blocks.

The upper side walls and roof of the glass tank are constructed of silica brick, which are often used for the ports. Kaolin forsterite and kyanite brick are finding increasing use in the upper parts of the tank.

In Table 132 is shown a classification of refractories used in the bottle-glass furnace together with their operating conditions. It is rather difficult to give any figures on the life of refractories in the glass-tank operation because it is so dependent on the type of glass, melting conditions, etc. It is usual, however, to run a continuous glass tank for 6 months to two years before the blocks wear so thin that a shutdown is necessary. The usual soda-lime glass of window or bottle composition is not so active in attacking the blocks as the borosilicate glass or the opal glass.

The tendency is to use more and more insulation in the upper parts of the modern glass tank. It is now standard practice to insulate the regenerator chambers and often the uptakes and side port walls as well. Quite a number of insulated crowns are in use at the present time, but this construction is still viewed with suspicion by many operators.

Tank Blocks. The demands on the flux blocks in the glass tank are particularly exacting, as the blocks are in contact continuously with the molten glass; and especially in portions where the movement of the glass is rapid, such as at the metal line and through the throat blocks, the attack is severe. Blocks for this service must have a low porosity, and particularly they must be free from flaws and laminations, which serve as an entering wedge for the glass erosion. Some believe that it is more important to have the pores all below a certain size than to have a minimum porosity, because apparently the surface tension of the glass will not permit it to enter pores below a critical size. Therefore, experience has shown that certain types of block, even with medium porosity, give good results if the pore size is very small. On the other hand, blocks with practically zero porosity made by casting the molten materials give good resistance to certain types of glass.

The chemical composition of the block does not seem to be so important as the physical characteristics. However, blocks made of mullite or alumina appear in general to have a resistance superior to those made of fireclay mixtures. Certain types of refractory, *e.g.*, chromite, that would be quite resistant to the glass cannot, of course, be used because of the color imparted to the glass, but chromite can be added in small amounts to fused Al_2O_3 blocks.

Glass Pots. The glass pot for melting glass is made of a carefully prepared fireclay-and-grog mixture with particular care to get a homogeneous structure. This is accomplished in modern practice by slip casting the

pot in one piece from a high-density slip carefully deflocculated to give sufficient fluidity for pouring. The pot must have sufficient mechanical strength and resistance not to creep at high temperatures so that the heavy load of glass will be supported without failure of the refractory. Here again it is difficult to give any definite figures on the life of the pot because it depends so much on the batch melted, the method of heating, and the type of fuel. However, pots often last for 10 to 20 melts before failure. In the manufacture of optical glass, the pot is used only once, because the batch and pot are cooled together and the pot is cracked away from the solidified glass.

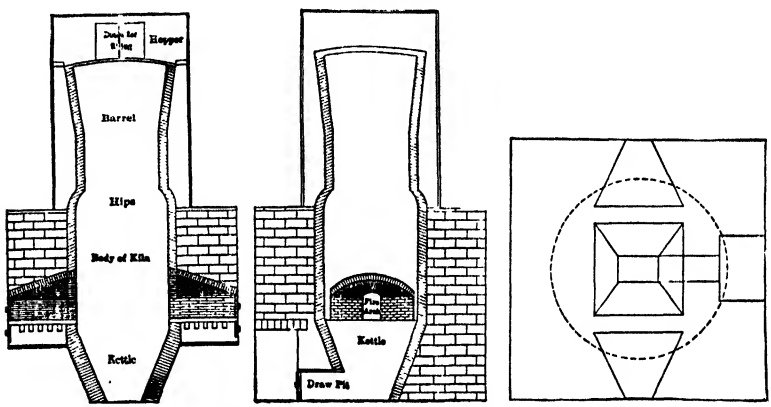


Fig. 378. A lime kiln. (*Reprinted by permission from "Cements, Limes and Plasters" by Eckel, John Wiley & Sons, Inc.*)

3. Refractories in the Cement and Lime Industry. *Shaft Kilns for Lime Burning.* All the lime was burned in shaft kilns in early days; and even now, the smaller plants use this type of kiln. As shown in Fig. 378, the kiln consists of a vertical shaft into which the raw material is fed at the top and the burned material pulled out at the bottom. Coal-fired grates supply the hot gases necessary for the burning operation.

These kilns are lined with a dense fireclay brick to stand the abrasion of the moving charge; but recently, super-duty fireclay brick have been used successfully for high-temperature parts. Success has often been obtained by using silica brick around the eyes of the kiln.

Rotary kilns are now used for burning lime in the larger plants and, in construction, are very similar to kilns for Portland cement manufacture. The lining of these kilns is usually made of super-duty fireclay block or high-alumina block. For the hot zone, magnesite blocks have been successfully used with steel-sheet inserts between the individual blocks.

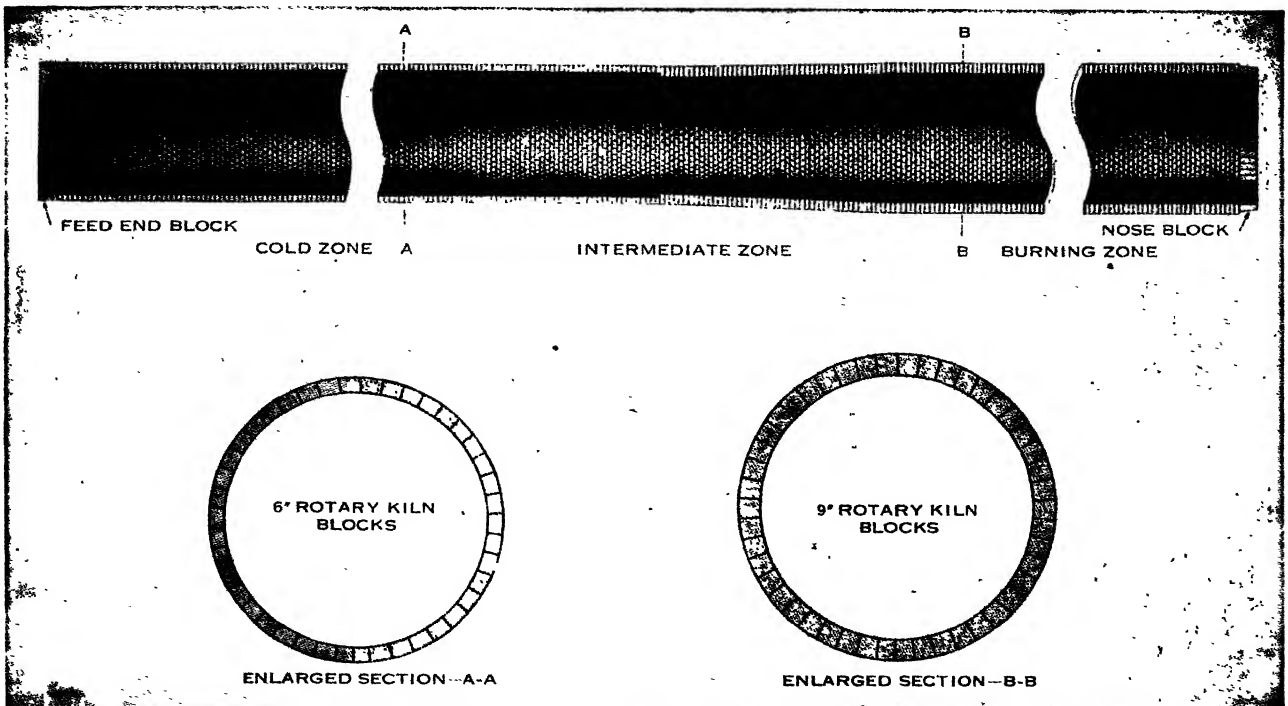


FIG. 379. Rotary cement-kiln lining. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

Kilns for the Manufacture of Portland Cement Clinker. Portland cement is made from a mixture of limestone and clay, cement rock, or slag, which will give approximately the following composition:

	Per Cent
SiO_2	23
Fe_2O_3	3
Al_2O_3	8
CaO	63
MgO	2
SO_3	1

Two general processes are in use: In one, the raw materials are dried, ground, and fed into the kiln as a powder. In the other, the materials are wet ground and fed into the kiln as a slurry. Most of the Portland cement manufacture in this country is carried out with the dry process; whereas in Europe, the wet process is favored. As far as the refractories are concerned, there is no great difference between the two methods.

The rotary kiln lining, as shown in Fig. 379, is composed of special blocks usually of high-alumina material. In the hot end of the kiln, blocks are 9 in. thick; whereas in the cooler end, they are 6 in., and often insulation is used back of them in this portion. The temperature at the hot end of the kiln is rather high, reaching as much as 3000°F (about 1650°C), but there is little spalling. At the cool end of the kiln, the charge abrades the lining to some extent; and in the hot end, the clinker, which becomes soft, builds up a layer on the refractories and, under proper operating conditions, protects them from slag attack and abrasion; *i.e.*, the most satisfactory refractory is one that will best hold this layer of clinker. Recently, kiln linings of chemically bonded magnesite brick have proved very satisfactory, as might be expected from the basic character of the clinker. In Table 133 are given the common sizes of rotary kilns for cement manufacture.

4. Gas Production. *By-product Coke Ovens.* In this type of oven, the coking is carried out in a narrow chamber 16 to 22 in. wide, 10 to 12 ft high, and 30 to 36 ft long. The bituminous coal is fed in at the top until the chamber is full; then the coking takes place by heat applied to the outer walls of this chamber. After the coking has been finished, the charge is pushed out of the chamber laterally and at once quenched. The gases escaping during the coking period (12 to 30 hr) are collected in a large main and treated for removal of the by-products. A section of the Koppers type of by-product coke oven is shown in Fig. 380. It will be seen that the heating is regenerative, the gas usually being supplied by the coking process itself.

The walls of the coking chamber are comparatively thin to give low thermal resistance and therefore must have good mechanical strength The refractory used is silica brick, the pores of which are more or less filled with coke after long operation. The bricks must, of course, be quite resistant to the abrasion of the entering and leaving charge, and

TABLE 133. USUAL SIZES OF ROTARY KILNS
(From "Portland Cement" by Meade)

Inside diameter, ft.	Length, ft.	Capacity, bbl. per day
6	60	200
7	100	430
8	125	625
9	150	1,100
9	175	1,430
9	200	1,775
10	175	
10	200	1,775
10	250	
11	250	

there is a very rapid temperature change when the coal is dropped into the red-hot oven chamber. Care must be taken not to allow the temperature to drop to the critical temperature for silica brick. Sometimes fireclay brick are used at the end of the ovens where spalling may occur. Table 134 gives a survey of the conditions of the refractory in this type of oven.

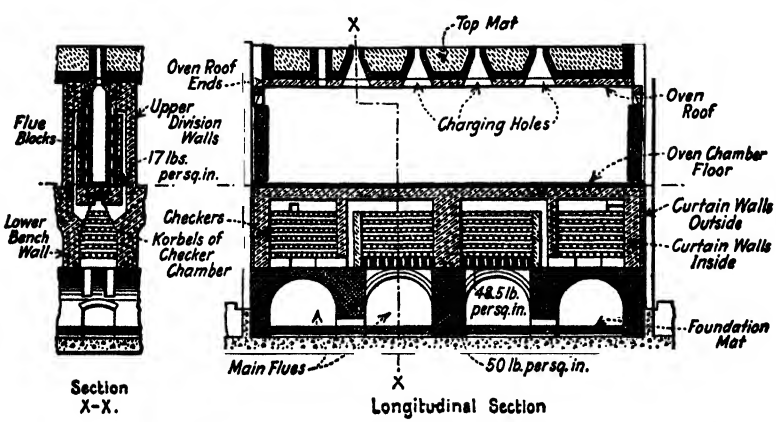


FIG. 380. By-product coke oven. (*Courtesy of American Refractories Institute.*)

TABLE 134. CLASSIFICATION OF REFRACTORIES FOR BY-PRODUCT COKE OVENS

(From "Manual of ASTM Standards for Refractory Materials")

Part (See Fig. 380)	Material used	Temperature*	Slagging	Load as given for Koppers ovens lb. per sq. in.	Load conditions in Semet-Solvay ovens	Abrasion	Spalling
Foundation mat	Fireclay brick	1830°F. (1000°C.), max	No	25 to 30	Important	No	No
Main flues	Silica brick and fireclay brick	1000°F. (540°C.) extraordinary 1300 to 1400°F. (705 to 760°C.)	No	16 to 20	Important	No	No
Lower bench walls.	Silica brick	1830°F. (1000°C.), max.	No	18 to 20	Important	No	No
Corbels of checker chambers	Silica brick	1830 to 2550°F. (1000 to 1400°C.)	No	20 to 25	Important	No	No
Checkers	Fireclay brick and silica brick	1830 to 2730°F. (1000 to 1500°C.)	No	8 to 10	No	No	No
Curtain walls inside	Silica brick	1830 to 2550°F. (1000 to 1400°C.)	No		No	No	No
Curtain walls outside	Fireclay brick	390 to 1830°F. (200 to 1000°C.)	No		No	No	No
Upper division walls	Silica brick	1830 to 2550°F. (1000 to 1400°C.)	No	12 to 15	Important	No	No
Flue blocks	Silica brick	2190 to 2730°F. (1200 to 1500°C.)	No		Important	Important	No
Oven chamber floor	Fireclay brick	1830 to 2190°F. (1000 to 1200°C.)	No	3 to 6	No	Important	No
Oven roof	Silica brick	1830 to 2190°F. (1000 to 1200°C.)	No	6 to 10	Important	No	No
Oven roof ends	Fireclay brick	1830 to 2190°F. (1000 to 1200°C.)	No	5 to 10	Important	No	No
Charging holes	Fireclay brick	1470 to 2190°F. (800 to 1200°C.)	No		No	Slight	No
Jamb blocks	Silica brick and fireclay brick	1830 to 2730°F. (1000 to 1500°C.)	No	15 to 20	No	Important	Important
Top mat	Fireclay brick	1110 to 1830°F. (600 to 1000°C.)	No	5 to 10	No	No	No

* The equivalent centigrade temperatures given in parenthesis are to the nearest five degrees.

Water-gas Generation. Gas produced in this manner takes place by the following process: A chamber filled with a bed of hot coal has air blown through it to increase its temperature and produce a gas of nitrogen, carbon dioxide, and carbon monoxide, which is burned in a second chamber called a "carburetor" partially filled with checker bricks, thus raising their temperature. Sometimes a second checkerwork is used as a preheater. The second part of the cycle consists in shutting off the air

blast and passing steam through the hot coal, which gives off hydrogen and carbon monoxide. This passes through the carburetor, where it is preheated and enriched by the gas produced by spraying oil on to the hot checkers. As soon as the checkerwork is cooled to a predetermined value, the cycle is repeated. In Fig. 381 is shown a cross section of a typical water-gas generator operating on this principle. The refractories used are fireclay, as the temperature is not particularly high, but considerable resistance to spalling is necessary in the carburetor. Also, since

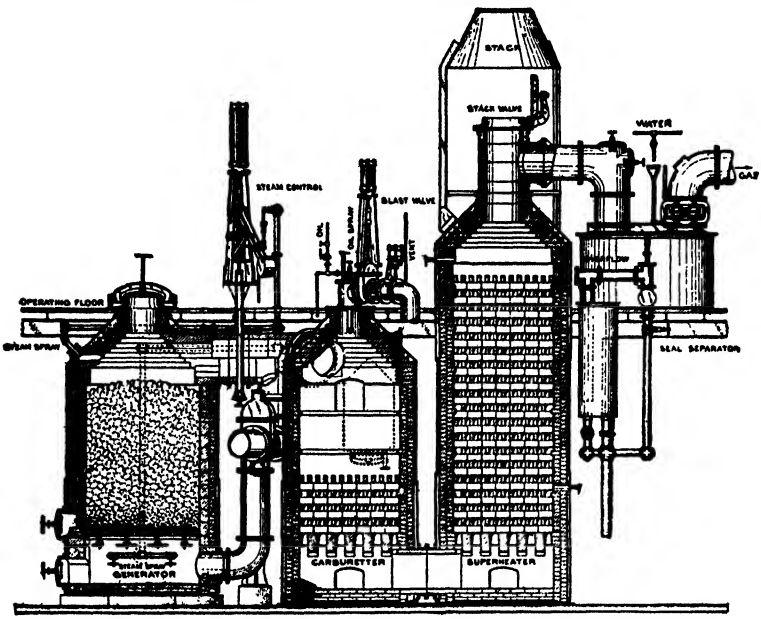


FIG. 381. Carbureted water-gas machine, Champaign. (*From C. W. Parmelee, A. E. R. Westman, and W. H. Pfeiffer, University of Illinois, Engineering Experiment Station.*)

the conditions for the most part are highly reducing, the bricks must be capable of withstanding the disintegrating effects of hydrogen and carbon monoxide.

5. Incinerators. Incinerators are used extensively for combustion of refuse and require refractories capable of standing sudden temperature changes, but they need never undergo very high temperatures. Therefore, a low-heat-duty brick with good spalling resistance is generally satisfactory.

6. Domestic Heating. The increasing use of oil burners for domestic heating has made a really large field for refractories, even though the number of bricks in any one unit amounts to only a few dozen. The temperatures in this service are low, but the bricks must be quite resistant

to spalling due to the intermittent action of the burner. In many types of installation, standard-size brick are used; but in a few cases, special shapes are assembled to reduce the labor cost.

The use of the insulating firebrick in this type of service has been increasing rapidly in the last few years because it permits a high temperature to be built up on the surface of the refractory immediately after the burner has started, so that efficient combustion takes place during the whole operation with less production of soot and lower consumption of oil. As the burner is in operation only for short periods of time, the immediate attainment of efficient combustion is very important. It has also been found that the sound-absorbing qualities of the porous insulating firebrick are very helpful in reducing the noise of the burner flame.

7. Paper-mill Refractories. *Sulfite Process.* For sulfur- and pyrite-burning furnaces, high-heat-duty or super-duty fireclay brick are generally employed.

Soda and Sulfate Processes. Refractories are required here for smelters, rotary incinerators, rotary and shaft kilns, and sludge recovery kilns. The slagging action is very severe in the smelting and recovery furnaces, as the soda salts are active fluxes. For the lower parts of these furnaces, soapstone or chrome brick are used, and dense high-heat fireclay brick are often employed in the upper portions. Black-liquor furnaces are discussed in Chap. XXIII.

8. Enameling. *Cast Iron.* Cast-iron enameling is generally carried out in recuperative-type muffle furnaces. The muffle, which is comparatively thin, is made of high-conductivity material, either silicon carbide or bonded alumina. The furnaces are generally underfired, and the refractory requirements of the piers holding up the hearth are rather severe, as the brick are heated all the way through and must carry a heavy load. For this purpose, high-burned kaolin or mullite brick have been found very satisfactory. The walls of the furnace itself are generally made of high-heat-duty firebrick, and insulation is often used outside this. Since the doors of these furnaces must be quick acting, they are often lined with a lightweight castable mixture or with insulating firebrick that are tied into the door casing. This not only permits a rapid operation of the door but makes conditions much more comfortable for the men working around the mouth of the furnace.

Sheet-steel Enameling. In this type of furnace, a muffle construction is used; but in many of the modern continuous furnaces, very little refractory is required, as the heat is supplied by radiant metal tubes inside which the combustion takes place. The walls of the furnace outside these tubes can readily be constructed of insulating firebrick, since the requirements in the way of temperature, load, and spalling are not at all severe.

CHAPTER XXVII

BRICKWORK CONSTRUCTION

1. Foundations. The foundations for kilns or furnaces are usually made of reinforced concrete to carry the usual engineering loads. These loads include not only the weight of the furnace itself and its charge but the thrust of the buckstay foot. As concrete loses considerable strength at temperatures above 400°C (about 750°F), it will be found necessary

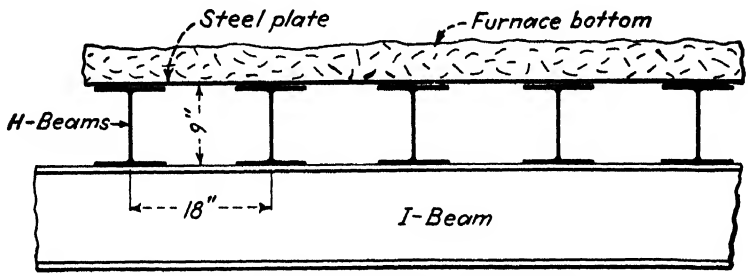


FIG. 382. Supports for an open-hearth bottom.

to protect the foundation from overheating if it is expected to maintain its full strength.

In some cases, the foundation is poured with a lightweight concrete containing a quartz-free aggregate. A mixture of crushed brickbats and high-alumina cement is generally preferred, a material that can be heated to elevated temperatures without cracking or entirely losing its strength, although it cannot be depended upon to support any concentrated loads. When reinforcing is used in foundations subjected to heat, the expansion characteristics of the high-temperature concrete and the reinforcing rods should be investigated to prevent a differential expansion from cracking the foundation.

In certain types of furnace, the bottom is supported directly on the steelwork. For example, the open-hearth furnace, a section of which is shown in Fig. 382, has the bottom on a steel plate which is supported by a series of H beams, thereby providing ventilation as well as a rigid support. The glass-tank bottom, as shown in Fig. 383, has the flux blocks supported directly on H beams, which permits the underside of the blocks to be air cooled.

2. Floors and Hearths. *Insulation.* The floor or hearth of a furnace is usually insulated from the concrete foundation, both to conserve fuel and to prevent overheating of the foundation. The insulation is often accomplished by putting down a layer of hollow tile on top of the concrete foundation. In other cases, discarded steel boiler tubes are set in the upper surface of the concrete foundation, a few inches apart, to allow ventilation. Another method uses a layer of cinders tamped over the concrete foundation, on top of which are laid several courses of firebrick. In the smaller furnaces, two or three courses of insulating brick may be laid on the concrete and then heavy brick placed on top of them. Many furnace designers do not appreciate the large amount of heat that may be lost through the foundations if the insulation is not well taken care of.

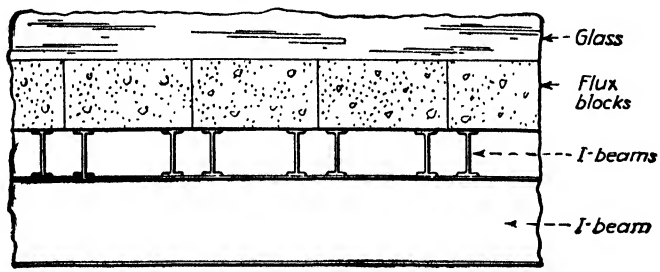


FIG. 383. Construction of the bottom of a glass tank.

Shapes and Bonds. Most of the hearth structures are laid with standard-size brick, a common type of construction being shown in Fig. 384. In some cases, however, larger blocks are used in the hearth to minimize the number of joints and to make larger units for reducing the tendency to float. In the case of the blast furnace, hearth blocks 18 × 9 × 4½ in. are generally used. Sometimes these bottoms are keyed in to prevent floating. In the case of glass tanks, the bottom is made of large flux blocks often 24 by 48 in. across the face. Here again, the purpose is to minimize the joints and prevent the bottom from floating.

Expansion Joints. It is just as important to have expansion joints in the hearth as in the walls, because failure to take care of this expansion will force out the base of the furnace and bend the buckstays or cause buckling of the bottom. The expansion joints may be put in the hearth, as shown in Fig. 384, although expansion joints directly under the walls are not considered good practice by some designers. The amount of expansion to be left is considered more fully under the section on walls.

Monolithic Construction. Many types of furnace hearth are constructed of a monolithic slab. The material may be magnesite grain as

in the open-hearth furnace, chrome plastic as in the bottom of a powdered coal-fired boiler, or beach sand as in a malleable-iron furnace. There are two general methods of putting in the monolithic material. The first is to place it in dry, perhaps with a little slag, and sinter it down in layers until a firm hearth is produced. The other method is to ram in the plastic mix while it is wet to a homogeneous structure, then dry it out, and fire it in place. Refractory concrete, made with either ordinary or

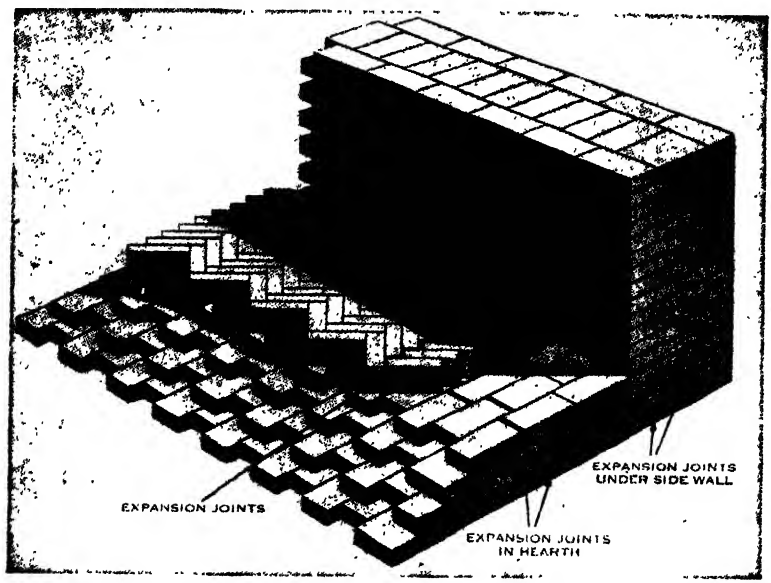


FIG. 384. Method of construction sometimes used in heating furnace bottoms. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

lightweight aggregate, is used to form monolithic hearths, particularly for car-bottom furnaces and tunnel-kiln cars.

3. Walls. The walls of a furnace are primarily for the purpose of retaining the heat in the working chamber. To be satisfactory, however, they must be stable under the severe operating conditions encountered. Experience has shown that certain limiting factors must be understood before satisfactory construction of walls can be accomplished.

Thickness. The thickness of the wall depends a good deal on the conditions encountered. From the point of view of stability, the higher walls must be thicker, as shown in Table 135. On the other hand, if the wall is subjected to severe slag attack or spalling, extra thickness must be built into it to give it a reasonable amount of life. Table 136 gives the number of brick required for various thicknesses of wall, both solid

and composite, data that will be useful in brickwork estimating. Table 137 gives the weight of various types of refractory for computing wall weights.

TABLE 135. SAFE WALL HEIGHTS FOR UNANCHORED WALLS

Wall Thickness, In.	Maximum Height* of Wall without Anchors but Arch Supported on Top of Wall, Ft.
4½	3
9	7
13½	12
18	15

* When wall does not support arch, the safe height is decreased 20 per cent.

Bonds. There are four ways of laying a standard brick, as indicated in Fig. 385. Nine-inch walls of one material are usually laid with all headers or with alternate header and stretcher courses. The rowlock courses are used for changing the height of the course, for sills, and for some floors but are not often used in wall construction with refractories. The soldier courses are not particularly stable and would not be used where they are expected to carry any amount of load. In building the thicker types of wall, it is necessary to bond the different layers together into a strong unit.

TABLE 136. WALLS MADE OF ONE KIND OF BRICK

Wall Thickness, In.	Number of Straight Brick per Sq. Ft.
2½	3.6
4½	6.4
9	12 8
13½	19.2
18	25.6
22½	32 0
27	38.4
36	51 2

Refractory Lining of a Composite Wall

9, fifth course tie	14
9, fourth course tie	14 4
4½, fourth course tie	8 0
4½, third course tie	8 5
4½, alternate header and stretcher	9 6
Alternate 9″ and 13½″ courses	16 0

Backing-up Insulation of a Compound Wall

9, fifth course tie	11.5
9, fourth course tie	11.2
4½, fourth course tie	4.8
4½, third course tie	4 26
4½, alternate header and stretcher	9.6
Alternate 9″ and 13½″ courses	16.0

Typical methods of bonding are shown in Fig. 386 for walls of different thickness. It should be noted that at the end of a wall, it is better to break the joint with a 6¾-in. brick, referred to as a large 9-in. straight, rather than with a soap, as this construction gives much greater stability.

TABLE 137. WEIGHT OF REFRACTORIES

Material	Weight per Cubic Foot
Fireclay brick	120–140
Super-duty brick	130–150
High-alumina brick:	
50	125–135
60	130–140
70	140–150
Fused Al_2O_3	153–196
Kaolin brick	130–135
Silica brick	100–110
Magnesite brick:	
Burned	160–175
Chemical bonded	180–185
Chrome brick:	
Burned	180–190
Chemical bonded	180–195
Silicon carbide brick	136–158
Forsterite brick	150–160
Insulating firebrick:	
1600°F	19–30
2000°F	28–40
2300°F	30–45
2600°F	39–55
2800°F	40–60
Insulating brick	20–35
Lightweight, castable	55–80 (45–75 fired)
Fireclay plastic	120–130
Chrome plastic	175–200
Mortar, high temperature	90–120
Mortar, chrome	125
1 cu. ft. of firebrick requires	seventeen 9-in. straights
1 cu. ft. of red brick requires	21 std. brick
1,000 firebrick closely packed occupy	60 cu. ft.

With composite walls, *e.g.*, a combination of heavy brick and insulating firebrick, it is necessary to tie one layer into the other. The general rule is that the tie should be made of the stronger layer, as it is less apt to break off. A number of methods of tying composite walls are shown in Fig. 387. In many cases, the tie brick can be made with soaps rather than straights when using an insulating-firebrick lining, which reduces the heat conductivity of the whole.

Many types of furnace construction are carried out with bricks larger

than the 9-in. size for more rapid laying of the brick or for more solid structures. The 3-in. brick series is commonly used; and in some of the steel furnaces, still larger units are found useful. It should be noted that the dimensions of the standard brick are not ideal for the purpose of efficient laying. Strictly speaking, the thickness of the brick should be definitely related to the width and length, so that the brick could be tied into the structure no matter in what position it was used. For example, if we consider the length of the brick 9 in. and use a $\frac{1}{16}$-in. joint, the dimensions would be $9 \times 4\frac{15}{32} \times 2\frac{15}{16}$. Under these conditions, a rowlock course would equal two stretcher courses and one soldier course would correspond

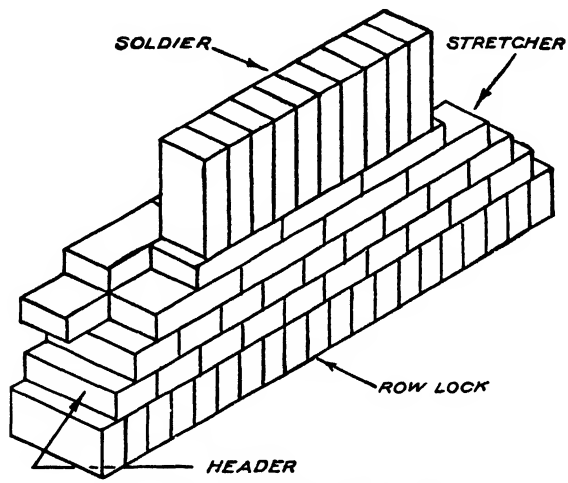


FIG. 385. Methods of laying brick.

exactly to three stretcher courses. It will be seen that the 3-in. brick closely fulfills these conditions.

Expansion Joints. All except the smallest refractory structures must have allowance made for expansion on heating. Considerable experience is necessary to know how many and what size expansion joints are to be used, but it is better to allow a little too much than not enough. An expansion joint in a wall can be a straight vertical joint, or it can be a broken joint, as shown in Fig. 388. In other types of construction, particularly when using silica and magnesite bricks, the expansion is taken care of by inserting a piece of cardboard in each vertical joint of the wall. This burns out and allows the individual bricks to expand freely.

When regular expansion joints are used, it is common in high-temperature furnaces to place them not more than 10 or 15 ft apart, usually at the corners of the furnace first and then in intermediate positions if

necessary. In Fig. 389 are shown typical expansion joints near a corner Figure 390 shows an expansion joint used with insulating firebrick inside a steel casing. If it is necessary to keep the expansion joints gastight, loosely

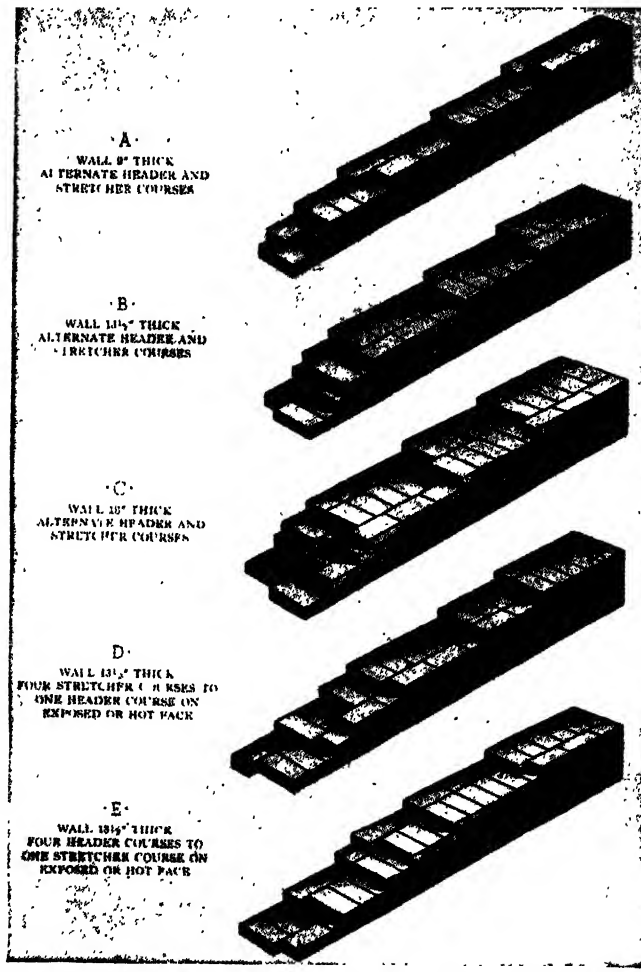


FIG. 386. Bonding of walls built with standard 9-in. brick. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

packed asbestos rope or mineral wool can be used on the cooler face to seal them entirely.

Horizontal expansion joints to allow for vertical expansion are sometimes required, as in sectionally supported walls and where the arch is supported independently of the walls.

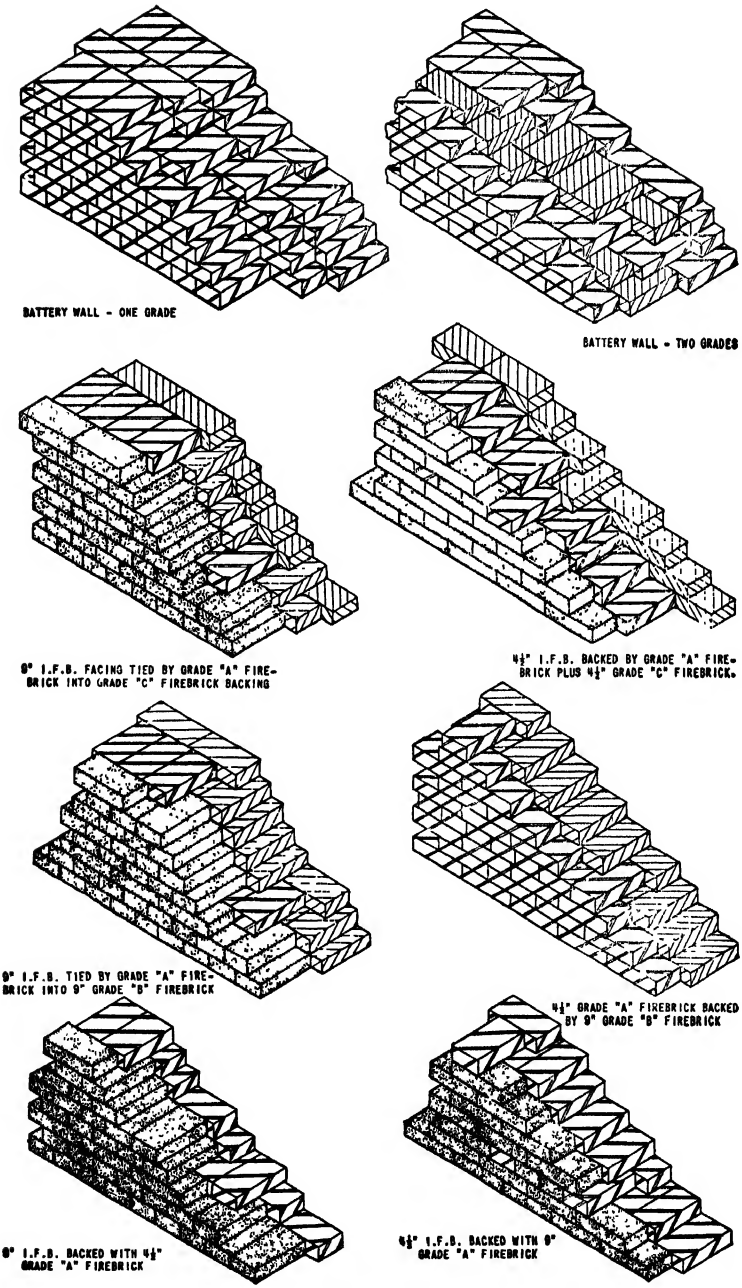


FIG. 387. Method of bonding composite walls. (*Courtesy of Babcock & Wilcox Company.*)

In Table 138 is given the width of expansion joints in inches per foot of wall for various types of refractory and at various temperatures.

TABLE 138. WIDTH OF EXPANSION JOINTS IN INCHES PER FOOT OF WALL LENGTH

Type of refractory	Maximum hot-face temperature			
	1500	2000	2500	3000
Fireclay	3/64	1/16	5/64	3/32
Magnesite	3/32	1/8	3/16	1/4
Silica	3/16	5/32	5/32	5/32
Chrome	1/16	5/64	3/32	5/32
Silicon carbide	1/32	3/64	1/16	5/64
Kaolin	1/32	3/64	1/16	5/64

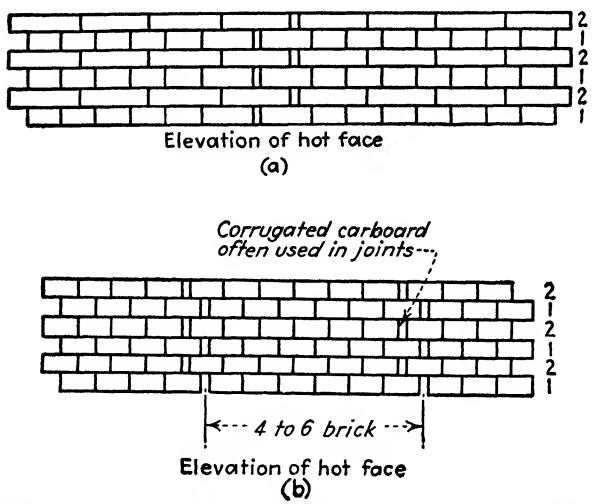


FIG. 388. Expansion joints in walls. (*a*) 13½-in. wall, alternate header and stretcher construction. (*b*) Built of magnesite brick, 9-in. header construction. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

Methods of Anchoring the Wall. When very thin or high walls are used, they must be anchored at certain intervals to the casing or steelwork to prevent buckling. The design of anchors has been greatly improved in the last few years and has thereby permitted the use of much thinner walls in many types of furnace. This anchoring is usually accomplished by a bolt fitting into a special brick. In Fig. 391 is shown one method of anchoring an insulating firebrick wall with a heavy brick tile. Figure 392 illustrates

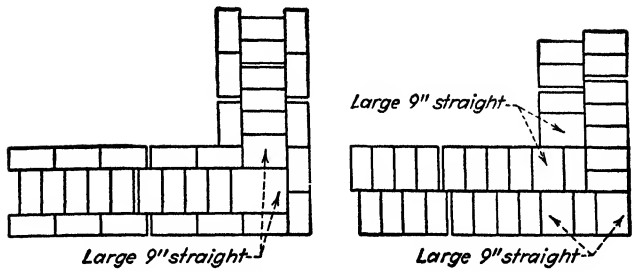


FIG. 389. Double expansion joint in wall near corner. 18-in. wall, alternate courses showing header and stretcher construction. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

another method, where a T-headed bolt fitting into a slotted brick makes an excellent construction.

The number of anchor bolts required for higher walls must be carefully worked out for efficiency and safety. The chart shown in Fig. 393 gives suggested vertical locations for anchor bolts in 9 in. thick walls.

High walls, such as those used in boilers, even when 18 to 22½ in. thick

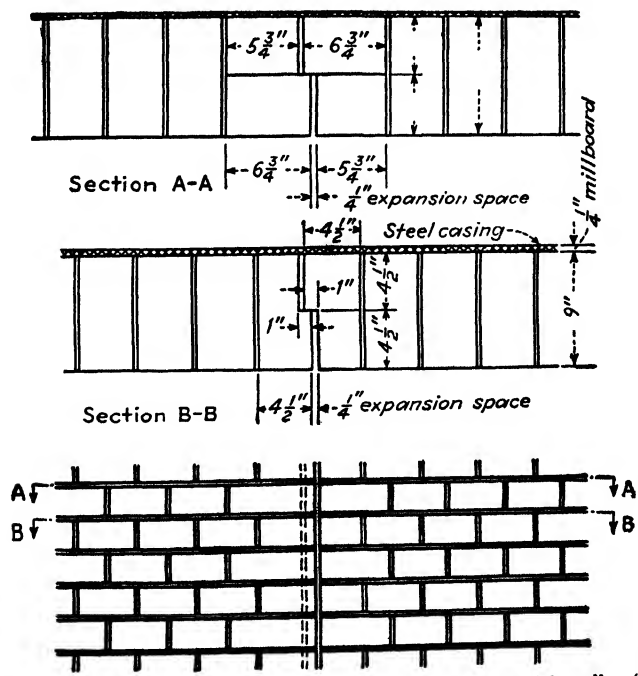


FIG. 390. Expansion joint arrangement, 9-in. thick insulating firebrick wall. (*Courtesy of Babcock & Wilcox Company.*)

must be anchored. This can be carried out by the use of special anchor tile as furnished by the various manufacturers.

Insulation. When insulation is applied to the outside of the wall, it may be tied in as shown in Fig. 387 or it may be placed between the refractory and a steel casing in the form of a block. In some types of construction, the outer face of the wall is made of red brick to protect the insulating material. This construction is stable, but it increases the heat storage of

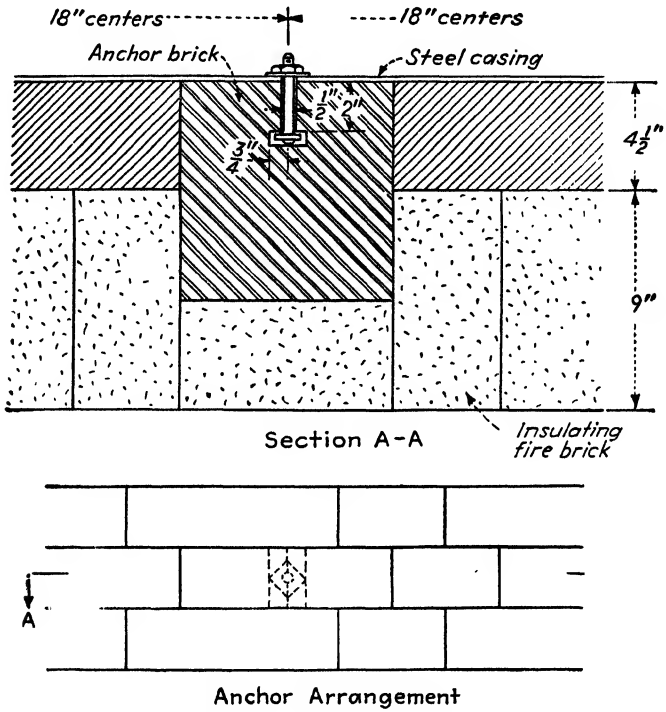


FIG. 391. Anchor arrangement. (*Courtesy of Babcock & Wilcox Company.*)

the wall, which is a disadvantage for intermittent operation, and also requires additional floor space. Many insulated furnaces simply have the corners protected with angle iron, and the face of the insulation is coated with a hard-face cement and possibly an asphalt coating for waterproofing. Another method of protecting the insulation is to use a casing of approximately 10-gage sheet steel or aluminum.

4. Doors, Ports, and Flues. *Door Openings.* The door openings in most furnaces are among the most troublesome points in the structure, both because they mechanically weaken the wall and because the door frame must take considerable abuse from charging and hot gases. One of the

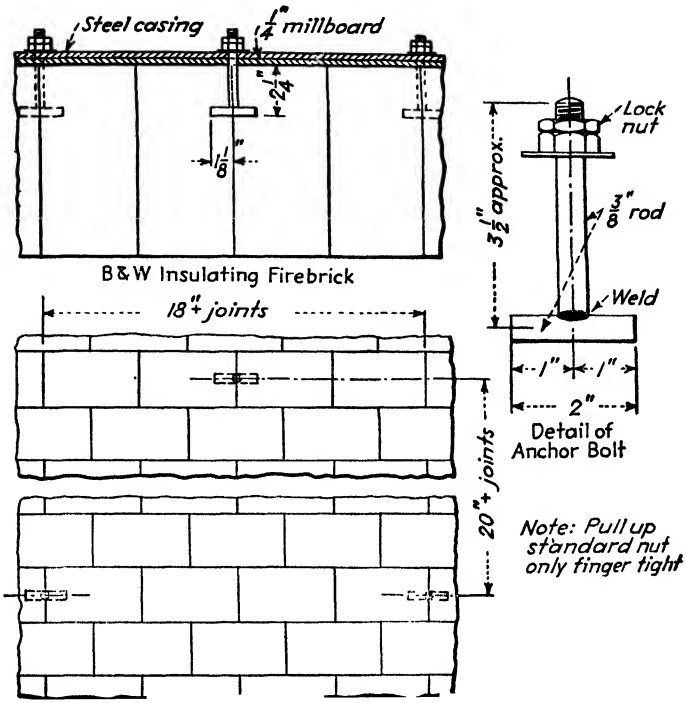


FIG. 392. Method of holding insulating firebrick to casing. (*Courtesy of Babcock & Wilcox Company.*)

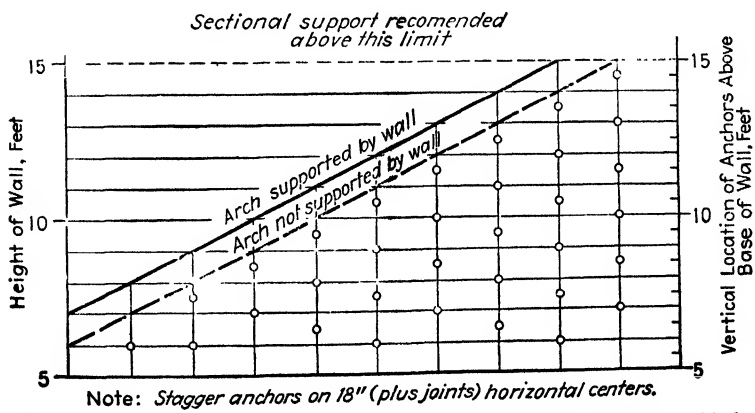


FIG. 393. Stagger anchors on 18-in. (plus joints) horizontal centers. (*Courtesy of Babcock & Wilcox Company.*)

first rules in door construction is to keep the width as small as possible compatible with access to the furnace. A typical door structure is shown in Fig. 394*a*, where a 4½-in. arch is thrown over the top of the opening and bonded into the wall. As the front 9-in. bricks are apt to be knocked loose, the sill of the door should be made of a solid construction. This may be accomplished by using a rowlock course bonded with air-setting mortar

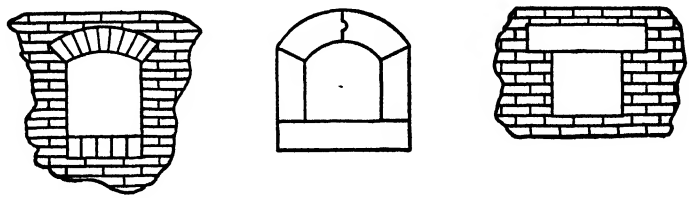


FIG. 394. Door openings.

or by using larger than 9-in. brick. Figure 394*b* shows a door opening, or port, of somewhat smaller size made up of special shapes, a construction that generally gives excellent service. In Fig. 394*c* is shown a wall opening with a heavy tile across the top. This construction, though satisfactory for low-temperature work, is to be avoided for high-temperature furnaces, as the tile usually cracks in the center and the broken ends sag.

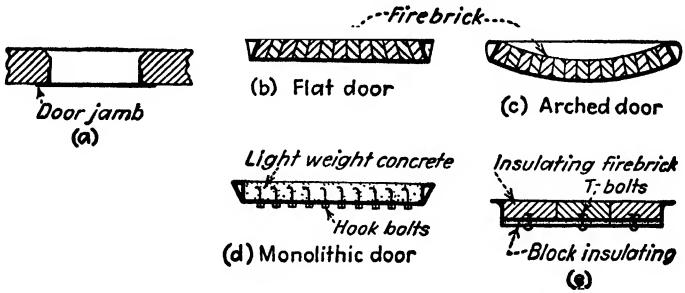


FIG. 395. Door construction.

In the low-temperature structures, a steel door jamb is often placed outside the wall to protect the brickwork. This is welded together from standard angle iron and makes a solid structure, as shown in Fig. 395*a*. For higher temperature furnaces, such as the open hearth, a water-cooled door jamb is generally used. It holds the brickwork in shape and resists to a considerable extent the abuse to which it is subjected from the charging machine.

Doors. Doors on furnaces almost always slide in vertical ways with a counterwieight to balance them approximately. The weight of the door

should be kept as low as possible in order to reduce the cost of the supports and make the operation quicker. Two general types of door are the flat door and the arch door, as shown in Figs. 395*b* and 395*c*, where the shapes are locked into the door frame to prevent them from bowing in. Such a door will stand considerable mechanical abuse, but it is rather heavy and conducts much heat out of the furnace.

More recently, furnace doors have been lined with lightweight concrete held in place by hook bolts as shown in Fig. 395*d*. This construction is very simple to reline, gives a light door, and has a comparatively low heat conductivity. Another construction for higher temperature use is shown in Fig. 395*e*, where the door is lined with insulating firebrick held into the door frame. This gives a lightweight construction and one that is an excellent insulator; the latter is a factor of great importance to the comfort of the men working around the furnace.

Ports and Burner Openings. Ports or openings in the furnace walls, when large, are constructed in the same way as described for the door openings. When the ports are smaller, a special shape often is set into the wall with the proper opening molded into it or a number of shapes are fitted together to form the opening, as would be the case in burner tile as shown in Fig. 396. It is often found practical to form the port or opening out of plastic material, which is rammed into place around the form in a rectangular opening in the brickwork. When properly made, such a construction often works out very satisfactorily and avoids the necessity of purchasing special shapes. Such plastic structures, however, are generally not so abrasion resisting as fired shapes and are not so satisfactory for extreme temperature conditions as preburned tile.

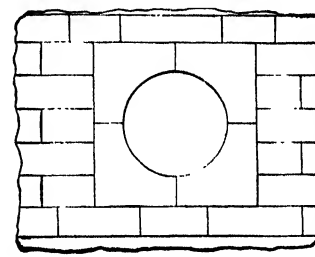


FIG. 396. Burner tile set in wall.

When walls are constructed of insulating firebrick, the ports or openings, when small, can often be cut directly in the wall after it has been finished. For larger openings, specially cut shapes can be used to advantage.

Flues and Ducts. Flues and ducts for high-temperature use are lined with a refractory. The smaller sizes are usually rectangular, and the larger ones circular, in which case arch or circle brick are generally employed. Where the moving gases in the duct do not carry a large amount of suspended particles, the ducts can well be lined with insulating firebrick, as a much thinner layer can be used because of its better insulating value. This, in turn, will allow a very much lighter lining, which means lower cost of steelwork and supports. The cost of the duct can often be cut in half by the use of insulating firebrick.

Stacks. Stacks for low-temperature furnaces are often of steel with a brick lining up to a sufficient distance to protect the steelwork. Insulating firebrick and lightweight concrete reinforced with wide-mesh, light-gage, expanded metal lath are frequently used for linings. For really high-temperature work, however, an all-brick stack is desirable such as that used for periodic kilns. Such a stack should have a firebrick lining that is free to expand and contract inside a stable wall such as is shown in Fig. 397.

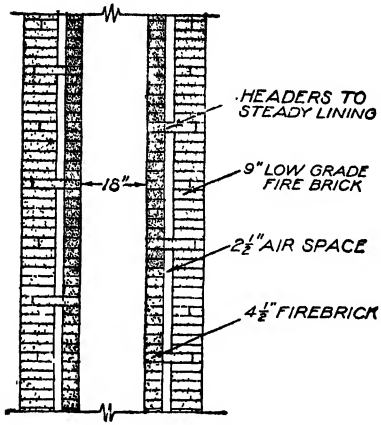


FIG. 397. High-temperature stack.

5. Sprung Arches. *Stresses and Shapes.* The circular arch, as generally employed, subtends an angle of 60 deg, which makes the radius of curvature equal to the span. However, there is no standardization in the ratio of span to rise of the arch, as in some cases a high arch is needed for combustion space and in others a very flat arch is desirable to force the flame down on the work. It should be noted that the circular arch in the higher forms becomes relatively unstable because of the fact that the line of

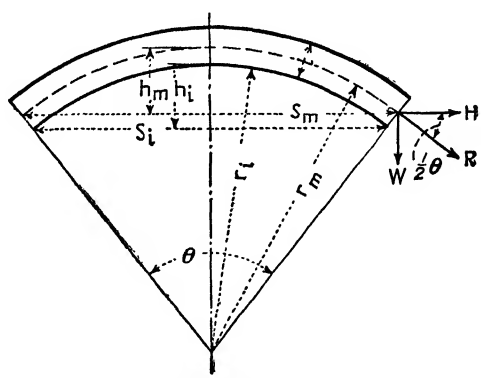


FIG. 398. Characteristics of the circular arch.

thrust of the arch takes the form of an inverted catenary which departs more and more from the circular form as the height of the arch increases. Therefore, it has been found desirable always to employ the catenary form of arch when the ratio of rise to span is large. The curvature of the circular arch is usually expressed in inches of rise per foot of span.

In Fig. 398 is shown a typical circular arch with the principal dimen-

sions given. From this diagram, it is easy to compute the various factors and stresses, which are given in the formulas below. It should be noted that for stress computations, the mean radius r_m must be used whereas for brickwork estimation, the inner radius r_i is more convenient. The rise, however, is the same in both cases, as $h_m/S_m = h_i/S_i$.

$$r_m = \frac{S_m^2}{8h_m} + \frac{h_m}{2}$$

$$h = r_m - \sqrt{r_m^2 - \left(\frac{S_m}{2}\right)^2}$$

$$\sin \frac{1}{2}\theta = \frac{S_m}{2r_m}$$

$$\tan \frac{1}{4}\theta = \frac{2h_m}{S_m}$$

$$W = \tfrac{1}{2}ltd$$

$$R = W \operatorname{cosec} \tfrac{1}{2}\theta$$

$$H = W \cot \tfrac{1}{2}\theta$$

$$l = 2\pi r_m \frac{\theta}{360}$$

where θ = the central angle
r_m = the radius at center of arch ring, ft
r_i = the inner radius of the arch ring
S = the span, ft
h = the rise, ft
t = the thickness, ft
W = one-half weight of 1-ft length of arch, lb
H = the horizontal thrust at skewback per foot of length, lb
R = the resultant thrust at skewback per foot of length, lb
l = the length of mean arc
π = 3.1416
d = the density of brick, lb/cu ft

In Table 139 are given the important factors applying to circular arches of various heights. This table will be found useful for the quick calculation of the characteristics of arches.

The temperature stresses in an arch are difficult to compute, but it may be said that they are greater in the flatter arches because a given expansion of the arch will produce a greater rise and more pinching of the tips of the bricks. To minimize this difficulty, especially with silica brick, tie bolts are often slacked off in a predetermined manner as the arch heats up in order to keep the curvature constant. There is also another temperature stress, due to the temperature gradient through the arch itself, thus causing the tips of the bricks to expand more than the outer face, which puts an

TABLE 139.

Inches rise per foot span	Central angle	Fraction of a complete circle	Weight factor, W_1	Horizontal-thrust factor, H_1	Resultant-thrust factor, R_1
1.000	37°51′	0.1051	1.02	2.90	3.07
1.250	47 04	0.1307	1.03	2.30	2.51
1.500	56 08	0.1560	1.04	1.87	2.13
1.608	60 00	0.1667	1.05	1.73	2.00
1.750	65 02	0.1807	1.06	1.57	1.86
2.000	73 44	0.2048	1.07	1.30	1.64
2.250	82 13	0.2284	1.09	1.15	1.52
2.500	90 29	0.2513	1.12	1.00	1.44
3.000	106 15	0.2952	1.16	0.76	1.25
6.000*	180 00	0.5000	1.57	0.00	1.00

* Unstable.

To find the weight of the roof multiply together the mean span, length, thickness (in feet), weight per cubic foot, and the factor W_1.

To find the horizontal thrust on one skewback multiply the factor H_1 by one-half the total weight.

To find the resultant thrust on one skewback multiply the factor R_1 by one-half the total weight.

additional compression force on the inner surface. This latter effect can be minimized by using insulation on the outside of the arch.

The catenary shape has been found particularly satisfactory for some of the higher arches, thus allowing the side walls and crown to be one con-

FIG. 399. Catenary. (*Courtesy of Babcock & Wilcox Company.*)

tinuous curve with almost complete elimination of ironwork, as shown in Fig. 399. The calculation of the catenary can be carried out as follows.

The equation of the catenary as illustrated in Fig. 400 is

$$y = \frac{m}{2}\left(e^{x/m} + e^{-x/m}\right)$$

or in hyperbolic functions

$$y = m \cos h \frac{x}{m}$$

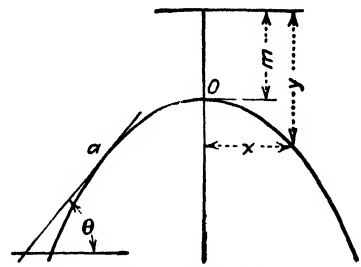


FIG. 400. Catenary.

The latter form is the most convenient to work with.

The slope angle at any point on the curve is given by

$$\theta = \tan^{-1}\left(\sin h \frac{x}{m}\right)$$

The length of the curve between the apex and any point is

$$l = m \sin h \frac{x}{m}$$

The radius of curvature at any point is

$$r = \frac{y^2}{m}$$

The compression (or tension) at the apex is

$$H = wm$$

where w = the weight per unit length of the curve

Table 140 shows the calculation of a typical high-catenary arch.

TABLE 140.

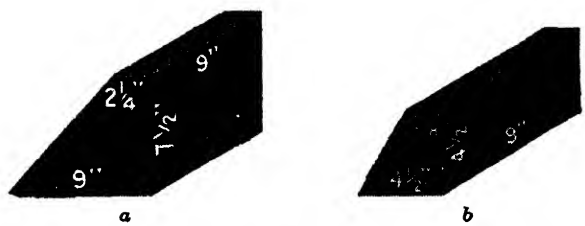
x	$\frac{x}{m}$	$\cos h \frac{x}{m}$	y	$y - m$
0	0	1.000	19.0	0
5	0.263	1.035	19.7	7
10	0.527	1.142	21.7	2.6
15	0.789	1.328	25.2	6.2
20	1.054	1.609	30.6	11.6
25	1.317	2.000	38.0	19.0
30	1.579	2.528	48.1	29.1
35	1.841	3.231	61.4	42.4
40	2.108	4.177	79.5	60.5
42	2.210	4.613	88.0	69.0

$m = 19$

It will be found, in general, more convenient to lay out the catenary by hanging a sash-weight chain along a vertical surface in such a way as to pass through the three points representing the skewbacks and the apex. The chain thus hanging will form a perfect catenary, and the shape can be traced from this directly on the surface.

Arch Spans and Thicknesses. It is a little difficult to give any hard-and-fast rules regarding the thickness and span of arches, as this ratio depends a great deal on the type of refractory, the temperature of the furnace, and the operating conditions. In general, for heavy brick construction, a 4½-in. thickness would not be used for more than a 5-ft span, a 9-in. arch would be used up to a 12-ft, a 13½-in. arch up to 16 ft, and an 18-in. arch up to 20 ft. However, there have been a number of successful operations at moderate temperatures with much wider arches than these. For example, a firebrick arch of 18-ft span and 9-in. thickness has given an excellent life.

In the case of the insulating-firebrick construction, the thickness is seldom over 9 in.; but in moderate-temperature construction, the span often is as great as 15 ft; and in one case, a 22-ft arch has given excellent service.



a *b*

FIG. 401. (*a*) Skewback built with standard 9-in. featheredge brick of the 2½-in. series. (*b*) Skewback built with standard 9-in. sideskew and endskew brick of the 2½-in. series. (*Courtesy of J. S. McDowell and L. L. Gill, "Steel."*)

Skewbacks. The skewback must be made to give the proper angle for the ends of the arch, and it must have sufficient face to accommodate the thickness of the arch ring. Standard skewbacks are made with side skews and featheredge bricks as shown in Fig. 401, which accommodate 4½ and 9½ in. thick arches with rises of respectively 1½ and 2$^{5}/_{16}$ in. per ft. However, special skewbacks can be readily obtained from most of the refractory manufacturers, as shown in Figs. 402 to 404, for an arch of 60-deg central angle. In the case of insulating-firebrick, standard skewbacks can be made up as shown in Fig. 405 out of standard shapes for arches having a 60-deg central angle. In the case of the insulating firebrick, however, it is very easy to grind the skewbacks to any desired slope.

Methods of holding the skewback are shown in Fig. 406, but in all cases, the arch thrust should be well supported by the ironwork using either an

angle section or a channel. As explained previously, the arch can be supported on top of the wall or supported independently of the wall. The latter construction would be used where the life of the side walls is shorter than the arch, such as in a glass tank, in which case a replacement of the walls can be readily made without disturbing the arch. Also, in the case of

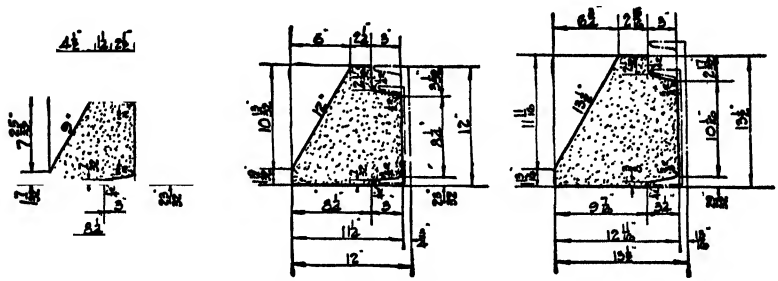


FIG. 402. Skewback brick with cutouts for steel channel framework. (*Courtesy of J. S. McDowell and L. L. Gill, "Steel."*)

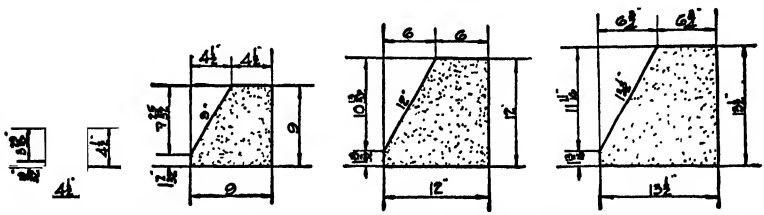


FIG. 403. Sixty-degree skewbacks. Shape 60–4½ is 9-in. thick; the others are 4½-in. thick. (*Courtesy of J. S. McDowell and L. L. Gill, "Steel."*)

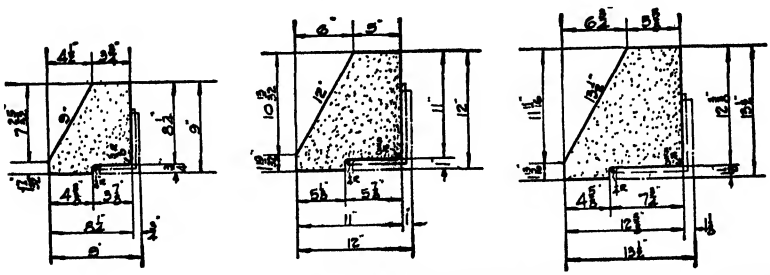


FIG. 404. Skewback brick with cutouts for steel angle supporting framework. (*Courtesy of J. S. McDowell and L. L. Gill, "Steel."*)

heavy arches, less load is put on the side walls if the arch is separately supported. On the other hand, wall-supported arches tend to hold the top of the wall from bowing in.

Steelwork. The steelwork for supporting the arch usually consists of an angle or channel running horizontally behind the skewback at the top of the wall; this is held in place by buckstays, the lower ends of which are held in

a socket in the concrete foundation and the upper ends tied together with a bolt. The section of iron used in the buckstays depends on the weight of the crown, a crown of insulating firebrick requiring much lighter sections than a heavy brick crown. The strength of these sections can be readily computed from the thrust of the arch, but a considerable factor of safety

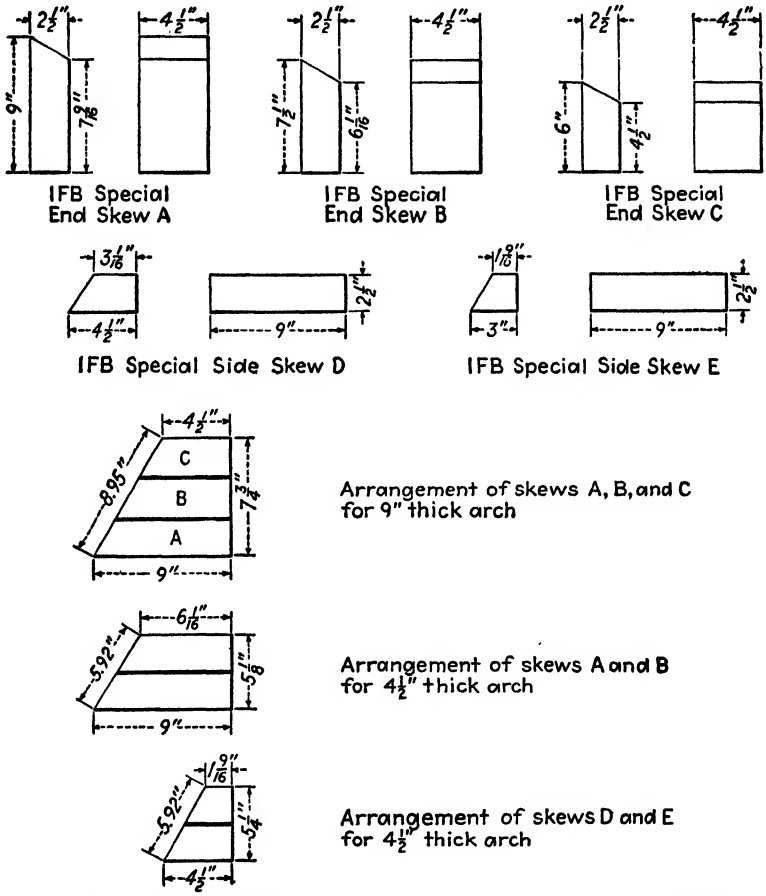


FIG. 405. Special IFB skewbacks for sprung arches in which the radius equals the span. Note: Mortar joints ⅛-in. thick. (*Courtesy of Babcock & Wilcox Company.*)

of at least 5 should be introduced because of the high temperature at which the buckstays go in certain types of construction.

The section of the buckstay has not received so much attention as it should. The I beam in (*A*) of Fig. 407 is the usual one because of its high mechanical efficiency. However, from the thermal point of view, it is most inefficient, as the inner flange is at a comparatively high temperature

whereas the outer flange is at a comparatively low temperature because of the small heat conductivity along the web. This condition produces a maximum of warping, which is often noticed in kiln construction, and thus

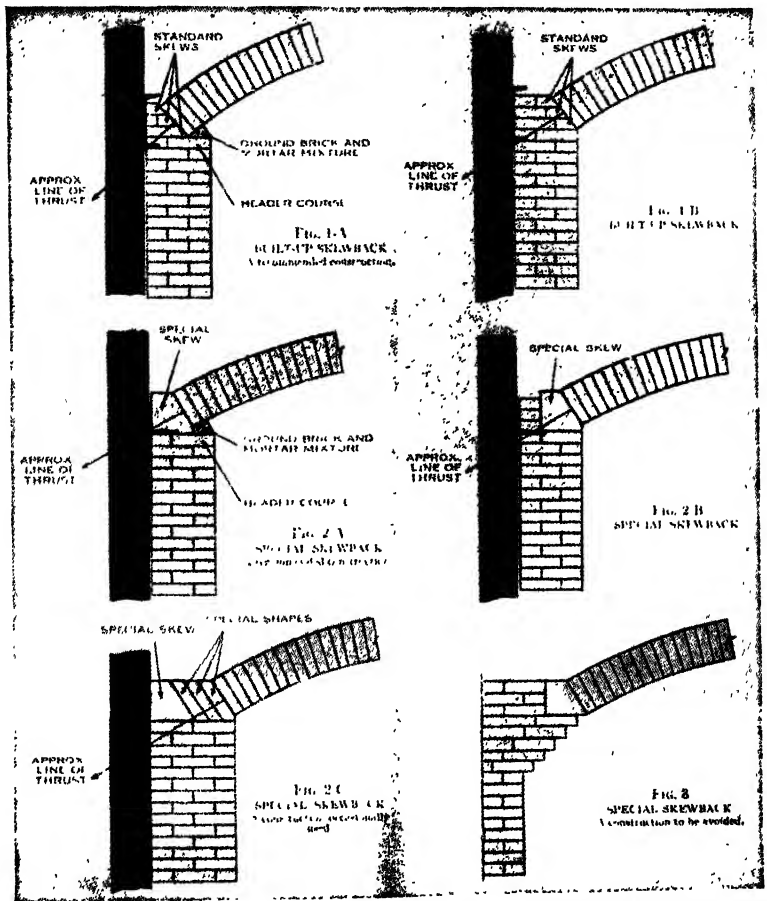


FIG. 406. Skewback construction. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

allows a bowing of the walls. A simple section (*B*) or a H section (*C*) will be found thermally more efficient because it will maintain a much more uniform temperature over the section.

Bonding of the Arch. Arches can be built up in a bonded construction, such as shown in Fig. 408, or in a separate ring construction, such as shown in Fig. 409. The bonded construction has the advantage of giving a more stable

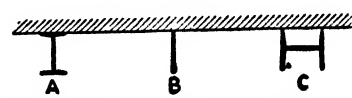


FIG. 407. Types of buckstay.

structure in case of failure of one or two individual units. On the other hand, it requires a little more skill in laying in order to get a uniform load on all the bricks. In the separate ring arch, any one ring can be repaired without disturbing the others, which in some cases is a real advantage.

Special Arches. There are many types of special arch, such as the rib arch in Fig. 410, often used in open-hearth-furnace crowns to give stability

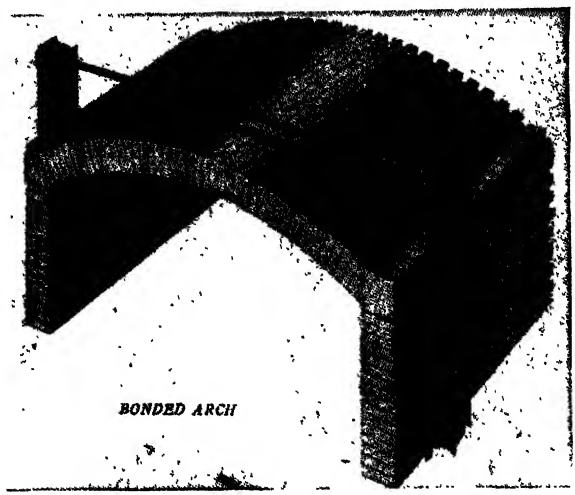


FIG. 408. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

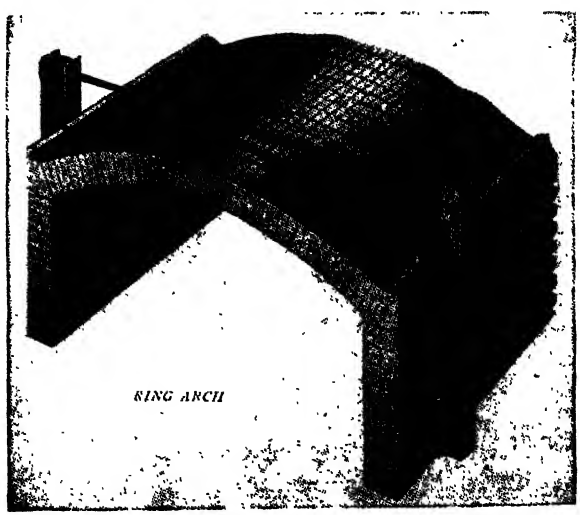


FIG. 409. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

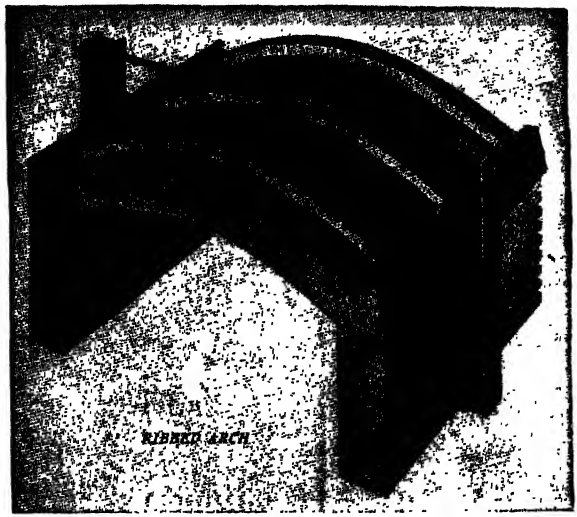


FIG. 410. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Company.*)

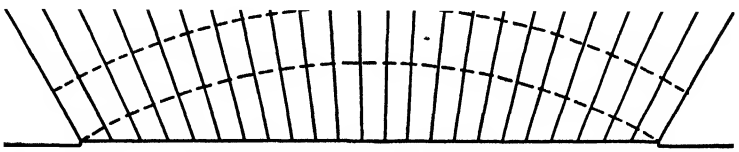


FIG. 411. Jack arch. This type of arch is formed by special wedge shapes, which may be designed by first laying out a radial sprung arch of proper rise and thickness for the given span, then extending all brick shapes upward to the level of the upper crown surface and downward to the spring line. This arch is designed on a basis of 1½-in. rise per foot of span. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Co.*)

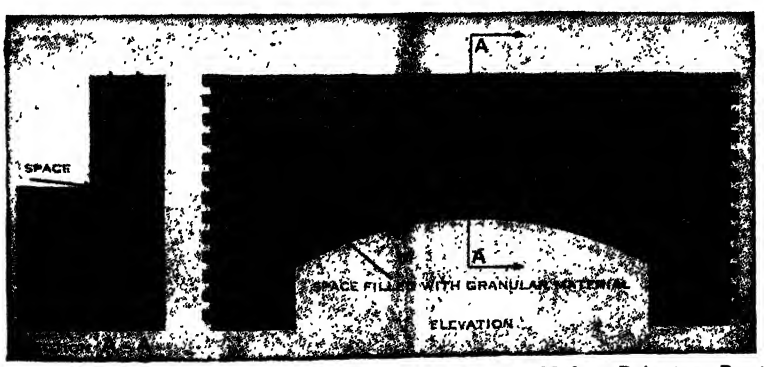


FIG. 412. Use of relieving arch to support wall. (*From "Modern Refractory Practice," courtesy of the Harbison-Walker Refractories Co.*)

TABLE 141. 9 × 4½ × 2½-IN. KEY BRICK*

Inside diameter	No. required to turn circle					
	No. 4 key	No. 3 key	No. 2 key	No. 1 key	Straight	Total
1′6″	26					26
2′0″	17	13				30
2′6″	9	25				34
3′0″		38				38
3′6″		29	13			42
4′0″		21	25			46
4′6″		13	38			51
5′0″		4	51			55
5′3″			57			57
5′6″			55	4		59
6′0″			50	13		63
6′6″			46	21		67
7′0″			42	30		72
7′6″			38	38		76
8′0″			34	46		80
8′6″			29	55		84
9′0″			25	63		88
9′6″			21	72		93
10′0″			17	80		97
10′6″			13	88		101
11′0″			9	96		105
11′6″			4	105		109
12′0″				113		113
12′6″				113	5	118
13′0″				113	9	122
13′6″				113	13	126
14′0″				113	17	130
14′6″				113	21	134
15′0″				113	26	139
15′6″				113	30	143
16′0″				113	34	147
16′6″				113	38	151
17′0″				113	42	155
17′6″				113	47	160
18′0″				113	51	164
18′6″				113	55	168
19′0″				113	59	172
19′6″				113	63	176
20′0″				113	68	181
20′6″				113	72	185
21′0″				113	76	189
21′6″				113	80	193
22′0″				113	84	197

TABLE 141. 9 × 4½ × 2½-IN. KEY BRICK* (*Continued*)

Inside diameter	No. required to turn circle					
	No. 4 key	No. 3 key	No. 2 key	No. 1 key	Straight	Total
22′6″				113	88	201
23′0″				113	93	206
23′6″				113	97	210
24′0″				113	101	214
24′6″				113	105	218
25′0″				113	109	222
25′6″				113	114	227
26′0″				113	118	231
26′6″				113	122	235
27′0″				113	126	239
27′6″				113	130	243
28′0″				113	135	248
28′6″				113	139	252
29′0″				113	143	256
29′6″				113	147	260
30′0″				113	151	264
30′6″				113	155	268
31′0″				113	160	273
31′6″				113	164	277
32′0″				113	168	281
32′6″				113	172	285
33′0″				113	176	289
33′6″				113	181	294
34′0″				113	185	298
34′6″				113	189	302
35′0″				113	193	306

* Applies also to 9 × 4½ × 3-in. key brick.

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire bricks; smaller fractions are disregarded.

for long spans. The jack arch in Fig. 411 is made up of special shapes in order to give a flat lower surface. This type of arch is often used in certain portions of tunnel kilns to conform closely to the charge.

The relieving arch shown in Fig. 412 is sometimes used to support the weight of an end wall and to take the load off the main arch. Relieving arches in modern construction are not used very extensively.

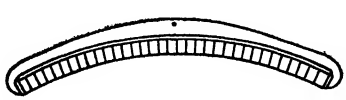


FIG. 413. Bung arch.

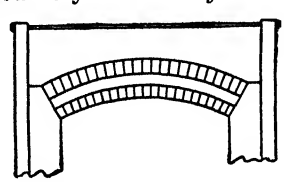


FIG. 414. Double arch.

TABLE 142. 9 × 4½ × 2½-IN. WEDGE BRICK*

Inside diameter	No. required to turn circle			
	No. 2 wedge	No. 1 wedge	Straight	Total
2′3″	57			57
2′6″	51	10		61
3′0″	38	30		68
3′6″	25	51		76
4′0″	13	71		83
4′6″		91		91
5′0″		91	7	98
5′6″		91	15	106
6′0″		91	22	113
6′6″		91	30	121
7′0″		91	38	129
7′6″		91	45	136
8′0″		91	53	144
8′6″		91	60	151
9′0″		91	68	159
9′6″		91	75	166
10′0″		91	83	174
10′6″		91	90	181
11′0″		91	98	189
11′6″		91	105	196
12′0″		91	113	204
12′6″		91	121	212
13′0″		91	128	219
13′6″		91	136	227
14′0″		91	143	234
14′6″		91	151	242
15′0″		91	158	249
15′6″		91	166	257
16′0″		91	173	264
16′6″		91	181	272
17′0″		91	188	279
17′6″		91	196	287
18′0″		91	203	294
18′6″		91	211	302
19′0″		91	219	310
19′6″		91	226	317
20′0″		91	234	325
20′6″		91	241	332
21′0″		91	249	340
21′6″		91	256	347
22′0″		91	264	355

TABLE 142. 9 × 4½ × 2½-IN. WEDGE BRICK* (*Continued*)

Inside diameter	No. required to turn circle			
	No. 2 wedge	No. 1 wedge	Straight	Total
22′6″		91	271	362
23′0″		91	279	370
23′6″		91	286	377
24′0″		91	294	385
24′6″		91	301	392
25′0″		91	309	400
25′6″		91	317	408
26′0″		91	324	415
26′6″		91	332	423
27′0″		91	339	430
27′6″		91	347	438
28′0″		91	354	445
28′6″		91	362	453
29′0″		91	369	460
29′6″		91	377	468
30′0″		91	384	475
30′6″		91	392	483
31′0″		91	399	490
31′6″		91	407	498
32′0″		91	415	506
32′6″		91	422	513
33′0″		91	430	521
33′6″		91	437	528
34′0″		91	445	536
34′6″		91	452	543
35′0″		91	460	551
35′6″		91	467	558
36′0″		91	475	566
36′6″		91	482	573
37′0″		91	490	581
37′6″		91	498	589
38′0″		91	506	597
38′6″		91	513	604
39′0″		91	521	612
39′6″		91	528	619
40′0″		91	536	627
40′6″		91	543	634
41′0″		91	551	642
41′6″		91	558	649
42′0″		91	566	657
42′6″		91	573	664

TABLE 142. 9 × 4½ × 2½-IN. WEDGE BRICK* (*Continued*)

Inside diameter	No. required to turn circle			
	No. 2 wedge	No. 1 wedge	Straight	Total
43'0"		91	581	672
43'6"		91	589	680
44'0"		91	598	689
44'6"		91	605	696
45'0"		91	612	703
45'6"		91	620	711
46'0"		91	627	718
46'6"		91	635	726
47'0"		91	642	733
47'6"		91	650	741
48'0"		91	657	748
48'6"		91	665	756
49'0"		91	672	763
49'6"		91	680	771
50'0"		91	687	778
50'6"		91	695	786

* Applies also to 9 × 6¾ × 2½-in. wedges and straights.

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

In Fig. 413 is shown a bung arch used in the malleable-iron industry. These arch rings are wedged tightly into a heavy iron frame so that they can be lifted off as individual units. Brick with good strength and spalling resistance are essential in this type of construction. In Fig. 414 is shown a double arch sometimes used in tunnel-kiln construction for preheating of the combustion air. This type of arch should never be used for high-temperature work because of the difficulty in making repairs on the inner arch.

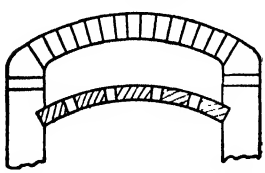


FIG. 415. Perforated arch.

Figure 415 shows a perforated arch used in some types of overfired furnace. As this arch is subjected to temperature on both sides, it must be made of material of high load-bearing capacity.

Expansion Joints. The longitudinal expansion joints in the crown should, in general, be aligned with the expansion joints in the wall. It is often desirable to recess the end of the crown into the end wall as shown in Fig. 416, giving a labyrinth joint. Expansion joints coming in the center of the crown should be covered with a row of splits cemented in place, also shown in Fig. 416.

TABLE 143. 9 × 4½ × 2½-IN. ARCH BRICK

Inside diameter	No. required to turn circle				
	No. 3 arch	No. 2 arch	No. 1 arch	Straight	Total
0′6″	19				19
1′0″	12	15			27
1′6″	4	30			34
1′9″		38			38
2′0″		34	8		42
2′6″		26	23		49
3′0″		19	38		57
3′6″		11	53		64
4′0″		4	68		72
4′3″			76		76
4′6″			76	4	80
5′0″			76	11	87
5′6″			76	19	95
6′0″			76	26	102
6′6″			76	34	110
7′0″			76	41	117
7′6″			76	49	125
8′0″			76	56	132
8′6″			76	64	140
9′0″			76	71	147
9′6″			76	79	155
10′0″			76	87	163
10′6″			76	94	170
11′0″			76	102	178
11′6″			76	109	185
12′0″			76	117	193
12′6″			76	124	200
13′0″			76	132	208
13′6″			76	139	215
14′0″			76	147	223
14′6″			76	154	230

TABLE 144. 9 × 4½ × 3-IN. WEDGE BRICK*

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
3′0″	57				57
3′6″	50	13			63
4′0″	44	26			70
4′6″	38	38			76
5′0″	32	50			82
5′6″	25	63			88
6′0″	19	76			95
6′6″	13	88			101
7′0″	6	101			107
7′6″		113			113
8′0″		107	13		120
8′6″		101	25		126
9′0″		94	38		132
9′6″		88	51		139
10′0″		82	63		145
10′6″		76	75		151
11′0″		69	88		157
11′6″		63	101		164
12′0″		57	113		170
12′6″		50	126		176
13′0″		44	139		183
13′6″		38	151		189
14′0″		32	163		195
14′6″		25	176		201
15′0″		19	189		208
15′6″		13	201		214
16′0″		6	214		220
16′6″			226		226
17′0″			226	7	233
17′6″			226	13	239
18′0″			226	19	245
18′6″			226	26	252
19′0″			226	32	258
19′6″			226	38	264
20′0″			226	45	271
20′6″			226	51	277
21′0″			226	57	283
21′6″			226	63	289
22′0″			226	70	296
22′6″			226	76	302

TABLE 144. 9 × 4½ × 3-IN. WEDGE BRICK* (*Continued*)

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
23′0″			226	82	308
23′6″			226	89	315
24′0″			226	95	321
24′6″			226	101	327
25′0″			226	107	333
25′6″			226	114	340
26′0″			226	120	346
26′6″			226	126	352
27′0″			226	133	359
27′6″			226	139	365
28′0″			226	145	371
28′6″			226	152	378
29′0″			226	158	384
29′6″			226	164	390
30′0″			226	170	396
30′6″			226	176	402
31′0″			226	182	408
31′6″			226	189	415
32′0″			226	195	421
32′6″			226	201	427
33′0″			226	208	434
33′6″			226	214	440
34′0″			226	220	446
34′6″			226	227	453
35′0″			226	233	459
35′6″			226	239	465
36′0″			226	246	472
36′6″			226	252	478
37′0″			226	258	484
37′6″			226	264	490
38′0″			226	271	497
38′6″			226	277	503
39′0″			226	283	509
39′6″			226	289	515
40′0″			226	296	522
40′6″			226	302	528
41′0″			226	308	534
41′6″			226	315	541
42′0″			226	321	547
42′6″			226	327	553

TABLE 144. 9 × 4½ × 3-IN. WEDGE BRICK* (*Continued*)

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
43'0"			226	334	560
43'6"			226	340	566
44'0"			226	346	572
44'6"			226	353	579
45'0"			226	359	585
45'6"			226	365	591
46'0"			226	372	598
46'6"			226	378	604
47'0"			226	384	610
47'6"			226	390	616
48'0"			226	397	623
48'6"			226	403	629
49'0"			226	409	635
49'6"			226	415	641
50'0"			226	421	647
50'6"			226	428	654

* Applies also to 9 × 6¾ × 3-in. wedges and straights.

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick: smaller fractions are disregarded.

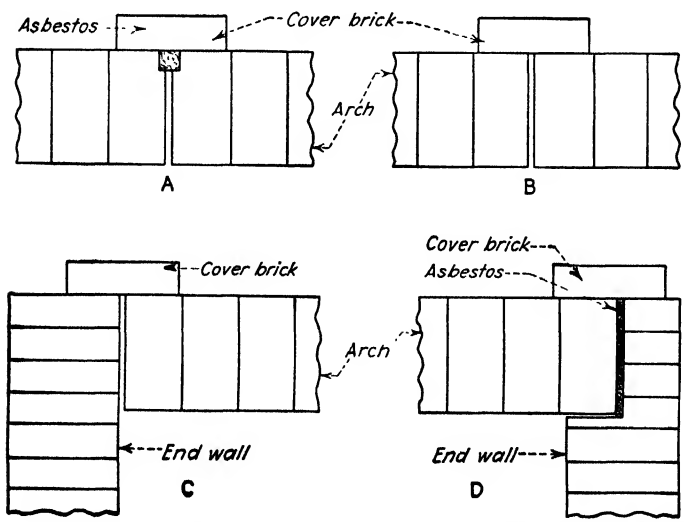


FIG. 416. Construction of expansion joints. (*Courtesy of the Babcock and Wilcox Company.*)

TABLE 145. 9 × 6 × 3-IN. KEY BRICK*

Inside diameter	No. required to turn circle			
	No. 2 key	No. 1 key	Straight	Total
6′0″	48			48
6′6″	45	6		51
7′0″	41	13		54
7′6″	38	19		57
8′0″	34	26		60
8′6″	31	32		63
9′0″	27	39		66
9′6″	24	46		70
10′0″	21	52		73
10′6″	17	59		76
11′0″	13	66		79
11′6″	10	72		82
12′0″	6	79		85
12′6″	3	85		88
13′0″		91		91
13′6″		91	4	95
14′0″		91	7	98
14′6″		91	10	101
15′0″		91	13	104
15′6″		91	16	107
16′0″		91	19	110
16′6″		91	22	113
17′0″		91	26	117
17′6″		91	29	120
18′0″		91	32	123
18′6″		91	35	126
19′0″		91	38	129
19′6″		91	41	132
20′0″		91	44	135
20′6″		91	48	139
21′0″		91	51	142
21′6″		91	54	145
22′0″		91	57	148
22′6″		91	60	151
23′0″		91	63	154
23′6″		91	66	157
24′0″		91	70	161
24′6″		91	73	164
25′0″		91	76	167
25′6″		91	79	170
26′0″		91	82	173
26′6″		91	85	176
27′0″		91	88	179
27′6″		91	92	183
28′0″		91	95	186
28′6″		91	98	189
29′0″		91	101	192
29′6″		91	104	195
30′0″		91	107	198

* Applies also to 9 × 6 × 2½-in. keys and straights.

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded

TABLE 146. 9 × 4½ × 3-IN. ARCH BRICK

Inside diameter	No. required to turn circle				
	No. 3 arch	No. 2 arch	No. 1 arch	Straight	Total
1′6″	29				29
2′0″	22	13			35
2′6″	16	25			41
3′0″	10	38			48
3′6″	3	51			54
3′9″		57			57
4′0″		54	6		60
4′6″		47	19		66
5′0″		41	32		73
5′6″		35	44		70
6′0″		28	57		85
6′6″		22	70		92
7′0″		16	82		98
7′6″		10	94		104
8′0″		3	107		110
8′3″			113		113
8′6″			113	4	117
9′0″			113	10	123
9′6″			113	16	129
10′0″			113	22	135
10′6″			113	29	142
11′0″			113	35	148
11′6″			113	41	154
12′0″			113	48	161
12′6″			113	54	167
13′0″			113	60	173
13′6″			113	66	179
14′0″			113	73	186
14′6″			113	79	192

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick, smaller fractions are disregarded.

TABLE 147. FLAT-BACK ARCH BRICK

Inside diameter	No. required to turn circle			
	No. 2 flat-back arch	No. 1 flat-back arch	Flat-back straight	Total
1′4″	26			26
1′6″	22	5		27
1′9″	16	14		30
2′0″	11	22		33
2′3″	5	30		35
2′6″		38		38
3′0″		38	8	46
3′6″		38	15	53
4′0″		38	23	61
4′6″		38	30	68
5′0″		38	38	76
5′6″		38	45	83
6′0″		38	53	91
6′6″		38	60	98
7′0″		38	68	106
7′6″		38	75	113
8′0″		38	83	121
8′6″		38	91	129
9′0″		38	98	136
9′6″		38	106	144
10′0″		38	113	151
10′6″		38	121	159
11′0″		38	128	166
11′6″		38	136	174
12′0″		38	143	181
12′6″		38	151	189
13′0″		38	158	196

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

TABLE 148. 12 × 6 × 3-IN. WEDGE BRICK

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
4′0″	76				76
4′6″	69	13			82
5′0″	63	25			88
5′6″	57	38			95
6′0″	51	50			101
6′6″	44	63			107
7′0″	38	75			113
7′6″	32	88			120
8′0″	25	101			126
8′6″	19	113			132
9′0″	13	126			139
9′6″	7	138			145
10′0″		151			151
10′6″		144	13		157
11′0″		139	25		164
11′6″		132	38		170
12′0″		126	50		176
12′6″		120	63		183
13′0″		113	76		189
13′6″		107	88		195
14′0″		101	100		201
14′6″		95	113		208
15′0″		88	126		214
15′6″		82	138		220
16′0″		76	151		227
16′6″		69	164		233
17′0″		63	176		239
17′6″		57	188		245
18′0″		51	201		252
18′6″		44	214		258
19′0″		38	226		264
19′6″		32	239		271
20′0″		25	252		277
20′6″		19	264		283
21′0″		13	276		289
21′6″		7	289		296
22′0″			302		302
22′6″			302	6	308
23′0″			302	13	315
23′6″			302	19	321
24′0″			302	25	327
24′6″			302	31	333
25′0″			302	38	340
25′6″			302	44	346
26′0″			302	50	352
26′6″			302	57	359
27′0″			302	63	365
27′6″			302	69	371
28′0″			302	75	377

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

TABLE 149. 13½ × 6 × 3-IN. WEDGE BRICK

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
4′6″	85				85
5′0″	79	13			92
5′6″	73	25			98
6′0″	66	38			104
6′6″	60	50			110
7′0″	54	63			117
7′6″	47	76			123
8′0″	41	88			129
8′6″	35	100			135
9′0″	29	113			142
9′6″	22	126			148
10′0″	16	138			154
10′6″	10	151			161
11′0″	3	164			167
11′3″		170			170
11′6″		167	6		173
12′0″		160	19		179
12′6″		154	32		186
13′0″		148	44		192
13′6″		141	57		198
14′0″		135	70		205
14′6″		129	82		211
15′0″		123	94		217
15′6″		116	107		223
16′0″		110	120		230
16′6″		104	132		236
17′0″		97	145		242
17′6″		92	157		249
18′0″		85	170		255
18′6″		79	182		261
19′0″		72	195		267
19′6″		66	208		274
20′0″		60	220		280
20′6″		53	233		286
21′0″		48	245		293
21′6″		41	258		299
22′0″		35	270		305
22′6″		28	283		311
23′0″		22	296		318
23′6″		16	308		324

TABLE 149. 13½ × 6 × 3-IN. WEDGE BRICK (*Continued*)

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
24′0″		9	321		330
24′6″		4	333		337
24′9″			340		340
25′0″			340	3	343
25′6″			340	9	349
26′0″			340	15	355
26′6″			340	22	362
27′0″			340	28	368
27′6″			340	34	374
28′0″			340	41	381
28′6″			340	47	387
29′0″			340	53	393
29′6″			340	59	399
30′0″			340	66	406
30′6″			340	72	412
31′0″			340	78	418
31′6″			340	85	425
32′0″			340	91	431
32′6″			340	97	437
33′0″			340	103	443
33′6″			340	110	450
34′0″			340	116	456
34′6″			340	122	462
35′0″			340	128	468
35′6″			340	135	475
36′0″			340	141	481
36′6″			340	147	487
37′0″			340	154	494
37′6″			340	160	500
38′0″			340	166	506
38′6″			340	172	512
39′0″			340	179	519
39′6″			340	185	525
40′0″			340	191	531
40′6″			340	198	538
41′0″			340	204	544
41′6″			340	210	550
42′0″			340	216	556
42′6″			340	223	563
43′0″			340	229	569

TABLE 149. 13½ × 6 × 3-IN. WEDGE BRICK (*Continued*)

Inside diameter	No. required to turn circle				
	No. 3 wedge	No. 2 wedge	No. 1 wedge	Straight	Total
43′6″			340	235	575
44′0″			340	242	582
44′6″			340	248	588
45′0″			340	254	594
45′6″			340	260	600
46′0″			340	267	607
46′6″			340	273	613
47′0″			340	279	619
47′6″			340	286	626
48′0″			340	292	632
48′6″			340	298	638
49′0″			340	304	644
49′6″			340	311	651
50′0″			340	317	657
50′6″			340	323	663
51′0″			340	330	670
51′6″			340	336	676
52′0″			340	342	682
52′6″			340	348	688
53′0″			340	355	695
53′6″			340	361	701
54′0″			340	367	707
54′6″			340	374	714
55′0″			340	380	720
55′6″			340	386	726
56′0″			340	392	732
56′6″			340	399	739
57′0″			340	405	745
57′6″			340	411	751
58′0″			340	418	758
58′6″			340	424	764
59′0″			340	430	770
59′6″			340	436	776
60′0″			340	443	783

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

TABLE 150. 13½ × 6 × 3-IN. KEY BRICK*

Inside diameter	No. required to turn circle			
	No. 2 key	No. 1 key	Straight	Total
6′0″	52			52
6′6″	48	7		55
7′0″	43	16		59
7′6″	38	24		62
8′0″	33	32		65
8′6″	28	40		68
9′0″	23	48		71
9′6″	18	56		74
10′0″	13	64		77
10′6″	8	73		81
11′0″	3	81		84
11′3″		85		85
11′6″		85	2	87
12′0″		85	5	90
12′6″		85	8	93
13′0″		85	11	96
13′6″		85	14	99
14′0″		85	18	103
14′6″		85	21	106
15′0″		85	24	109
15′6″		85	27	112
16′0″		85	30	115
16′6″		85	33	118
17′0″		85	36	121
17′6″		85	39	124
18′0″		85	43	128
18′6″		85	46	131
19′0″		85	49	134
19′6″		85	52	137
20′0″		85	55	140
20′6″		85	58	143
21′0″		85	61	146
21′6″		85	65	150
22′0″		85	68	153
22′6″		85	71	156
23′0″		85	74	159
23′6″		85	77	162
24′0″		85	80	165
24′6″		85	83	168
25′0″		85	87	172
25′6″		85	90	175
26′0″		85	93	178
26′6″		85	96	181
27′0″		85	99	184
27′6″		85	102	187
28′0″		85	105	190
28′6″		85	109	194
29′0″		85	112	197
29′6″		85	115	200
30′0″		85	118	203
30′6″		85	121	206
31′0″		85	124	209
31′6″		85	127	212
32′0″		85	131	216
32′6″		85	134	219
33′0″		85	137	222
33′6″		85	140	225
34′0″		85	143	228
34′6″		85	146	231
35′0″		85	149	234

* Applies also to 13½ × 6 × 2½-in. keys and straights.

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

TABLE 151. 9-IN. CIRCLE BRICK

Inside diameter	No. required to turn circle					
	24–33	36–45	48–57	60–69	72–81	Total
2′0″	12					12
2′3″	9	4				13
2′6″	6	8				14
2′9″	3	12				15
3′0″		16				16
3′3″		12	5			17
3′6″		8	10			18
3′9″		4	15			19
4′0″			20			20
4′3″			16	5		21
4′6″			10	12		22
4′9″			4	19		23
5′0″				24		24
5′3″				17	9	26
5′6″				12	15	27
5′9″				6	22	28
6′0″					29	29
	72–81	84–93	96–105	108–117	120–129	
6′3″	21	9				30
6′6″	14	17				31
6′9″	7	25				32
7′0″		33				33
7′3″		23	11			34
7′6″		14	21			35
7′9″		5	31			36
8′0″			37			37
8′3″			25	13		38
8′6″			18	21		39
8′9″			10	30		40
9′0″				41		41
9′3″				34	8	42
9′6″				23	20	43
9′9″				13	31	44
10′0″					45	45

TABLE 152. 9-IN. CUPOLA BLOCKS

Inside diameter	No. required to turn circle							
	A	B	C	D	E	F	G	H
1′4″	9							
1′6″	6	4						
1′9″		11						
2′0″		6	6					
2′3″			13					
2′6″				14				
3′0″				6	10			
3′4″					18			
3′6″					14	4		
4′0″					5	15		
4′3″						21		
4′6″						14	8	
5′0″							24	
5′6″							12	15
6′0″								20
6′1″								20

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

Brickwork Estimation for Sprung Arches. The sprung arch is made up of various combinations of straights, arches, wedges, or keys. The simplest method of finding the number of shapes in a given arch ring consists in determining the count needed for a complete circle in Tables 141 to 154 and then multiplying the number of each shape by the fraction of the circle covered by the arch as given in the third column of Table 139.

For example, let us find the number and kind of bricks in a 9-in. arch with an 11-ft span (S, of Fig. 398) and a rise of 1.608 in. per ft. Here the inner radius is equal to 11 ft; and from Table 142, it is seen that a circle of 22 ft inside diameter requires 91 No. 1 wedges and 264 straights. Multiplying these figures by the fraction of a circle 0.1667, the final count is 15 No. 1 wedges and 44 straights per ring. This calculation allows nothing for joints that may average $\frac{1}{32}$ to $\frac{1}{16}$ in. for the modern dipped joint.

The arch can be computed for any case without the tables by finding the total number of bricks in the ring, which is the outer arc in inches divided by 2.5 or 3.0 in. The number of tapered brick is found by dividing the difference between the inner and outer arcs in inches by the taper of a single brick in inches.

TABLE 153. 6-IN. CUPOLA BLOCKS AND 6-IN. ROTARY-KILN BLOCKS

Inside diameter	No. required to turn circle						
	30–42	36–48	42–54	48–60	54–66	60–72	66–78
2′6″	15						
2′9″	8	8					
3′0″		17					
3′3″		8	10				
3′6″			19				
3′9″			9	11			
4′0″				21			
4′3″				10	12		
4′6″					23		
4′9″					13	11	
5′0″						26	
5′3″						14	13
5′6″							28
	60–72	66–78	72–84	78–90	84–96	90–102	96–108
5′9″		16	13				
6′0″			30				
6′3″			18	13			
6′6″				32			
6′9″				19	14		
7′0″					34		
7′3″					16	19	
7′6″						36	
7′9″						17	20
8′0″							38
	90–102	96–108	102–114	108–120	114–126	120–132	123–135
8′3″		22	17				
8′6″			40				
8′9″			22	19			
9′0″				42			
9′3″				24	19		
9′6″					44		
9′9″					36	9	
10′0″						46	
10′3″							48

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

TABLE 154. 9-IN. ROTARY-KILN BLOCKS

Inside diameter	No. required to turn circle					
	48–66	54–72	60–78	66–84	72–90	78–96
4′0″	23					
4′3″	11	13				
4′6″		26				
4′9″		14	13			
5′0″			28			
5′3″			15	14		
5′6″				30		
5′9″				12	19	
6′0″					32	
6′3″					14	19
	72–90	78–96	84–102	90–108	96–114	102–120
6′6″		34				
6′9″		16	19			
7′0″			36			
7′3″			17	20		
7′6″				38		
7′9″				22	17	
8′0″					40	
8′3″					27	14
8′6″						42
	102–120	108–126	114–132	117–135	120–138	123–141
8′9″	25	18				
9′0″		44				
9′3″		27	18			
9′6″			46			
9′9″				48		
10′0″					49	
10′3″						50
	123–141	126–144	132–150	138–156	144–162	150–168
10′6″		51				
10′9″		14	38			
11′0″			53			
11′3″			24	30		
11′6″				55		
11′9″				34	22	
12′0″					57	
12′3″					24	34
12′6″						59

NOTE: Fractional parts of one-tenth of a brick or more are counted as entire brick; smaller fractions are disregarded.

When using insulating firebrick, it is often advisable to have them all ground with such a taper that the joints will all be radial. This construction, of course, makes the best type of arch.

Forms. Steel forms are to be preferred for arch construction that is often rebuilt. On the other hand, wooden forms are less expensive and quite satisfactory for one job. The forms are usually lagged with 2- by 2-in. oak strips.

The form should be accurately placed, with wedges or jacks for lowering. The arch should be built up from both skewbacks simultaneously to meet at the apex. The keys should be carefully fitted and not driven in too hard; otherwise the crown will be strained and the key cracked. Insulating-firebrick keys should never be hammered into place.

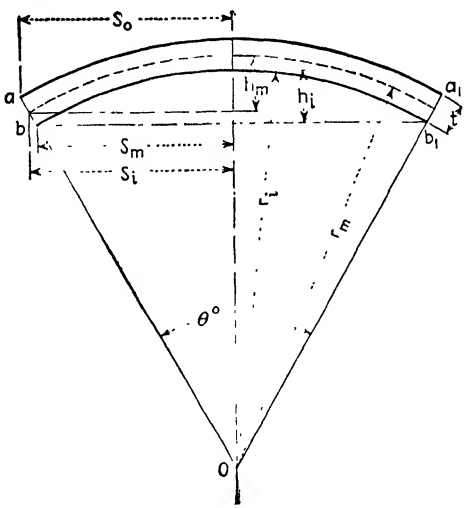


FIG. 417. Section of a dome.

6. Domes. *Stresses in Domes.* As the stresses in domes are redundant, it is difficult to obtain an exact evaluation. The band stress, however, is approximately given by

$$\frac{\text{Total weight of dome}}{\cos \frac{1}{2}\theta}$$

or

$$\frac{2\pi r_m h_m t d}{\cos \frac{1}{2}\theta}$$

in pounds

where d = the bulk density of the refractory, lb/cu in. The other symbols are shown in Fig. 417.

It should be noted that in the same way as for the cylindrical roof, the spherical dome is not the most stable form. Fellows[3] and Goodier[4] have shown that this limiting form approaches the surface of revolution formed by an ellipse. Any dome *inside* this surface is stable.

Brickwork Estimating. The dome can be constructed of radial blocks with a double taper to fit the particular radius used, or it can be made out of standard shapes such as straights, wedges, and keys, as is the usual practice in kiln construction. It will be seen, however, that perfect fitting cannot be obtained in either case and mortar must be used to make up the difference. The estimation of brick for the dome is a little complicated, but the following method will probably be found satisfactory for most cases.

With the Use of Special Blocks. The spherical dome can be best constructed of special shapes having a large end of 4½ by 2½ in. and a taper such that a projection of their corners will pass through the center of curvature of the dome. This allows strictly radial joints and either 2½- or 4½-in. rings. However, as the rings approach the top of the crown, even these blocks will not fit perfectly unless hand cut. In practice, such shapes can be economically made by grinding insulating firebrick, but with heavy bricks this is not generally feasible. Table 155 gives the dimensions of the small end of the bricks for 9 in. thick domes having various radii of curvature.

TABLE 155. RADIAL DOME BRICK

Size of dome, radius of curvature (inside surface)	Size of inner ends	
	Width, in.	Thickness, in.
4 ft. = 48 in.	3.79	2.11
6 ft. = 72 in.	4.00	2.22
8 ft. = 96 in.	4.12	2.29
10 ft. = 120 in.	4.18	2.33
14 ft. = 168 in.	4.28	2.37
18 ft. = 226 in.	4.33	2.40
24 ft. = 288 in.	4.36	2.42
30 ft. = 360 in.	4.39	2.44
40 ft. = 480 in.	4.42	2.45

With the Use of Standard Shapes. Most domes are built up in 2½-in. rings with combinations of straights and keys alternated with 4½-in. rings of straights and wedges to give the curvature in both directions. A by no means accurate fit can be obtained, and mortar must be used to fill the

joints. The estimation of the brickwork has been rather empirical, but the following method will give fairly close results.

Referring to Fig. 417, where a cross section of a typical dome is shown, the following relations are evident, all dimensions being in inches. It is assumed, as in the usual construction, that all the rings are 2½-in. wide.

The area of the outer surface of the dome

$$A = 2\pi(r_m + \tfrac{1}{2}t)h_m$$

Where h_m = the rise = $r_m - \sqrt{r_m^2 - s_m^2}$

The circumference of the segment at $a = 2\pi\left(r_m + \frac{1}{2}t\right) \cdot \sin\frac{1}{2}\theta$

The circumference of the segment at $b = 2\pi\left(r_m - \frac{1}{2}t\right) \cdot \sin\frac{1}{2}\theta$

$\frac{\text{Circumference at } a}{4.5}$ = number of 9-in. equivalents in first ring

$\frac{\text{Circumference at } a - \text{circumference at } b}{4.5 - 4.0}$ = number of No. 1 keys in first ring

$$\text{Arc } aa_1 = 2\pi\left(r_m + \frac{1}{2}t\right)\frac{\theta}{360}$$

$$\text{Arc } bb_1 = 2\pi\left(r_m - \frac{1}{2}t\right)\frac{\theta}{360}$$

$\frac{aa_1}{2.5}$ = number of rings

$\frac{aa_1 - bb_1}{2.50 - 1.88}$ = number of No. 1 wedge rings

The total number of 9-in. equivalents in the dome = $\frac{A}{4.5 \times 2.5} = \frac{A}{11.25}$

Of these $\frac{(aa_1 - bb_1)/(2.50 - 1.88)}{aa_1/2.5}$ are No. 1 wedges.

The remainder have $\frac{\text{circumference at } a - \text{circumference at } b}{4.50 - 4.0}$ / $\frac{\text{circumference } a}{4.5}$

No. 1 keys and the rest are straights.

Example of Dome Calculations:

Assume r_i = 120 in.

t = 9 in.

θ = 60 deg

Circumference of segment at $a = 2\pi(129) \cdot \frac{1}{2} = 406$ in.

Circumference of segment at $b = 2\pi(120) \cdot \frac{1}{2} = 377$ in.

$$\frac{406}{4.5} = 90 \text{ nine-inch equivalents in first ring}$$

$$\frac{406 - 377}{4.5 - 4.0} = \frac{29}{0.5} = 58 \text{ No. 1 Keys in first ring}$$

$$\frac{aa_1}{2.5} = \frac{129 \times 2\pi 1/6}{2.5} = 54 \text{ rings}$$

$$\frac{aa_1 - bb_1}{2.50 - 1.88} = \frac{129 \times 2\pi 1/6 - 120 \times 2\pi 1/6}{0.62} = \frac{135.2 - 125.9}{0.62}$$

$$= \frac{9.3}{0.62} = 15 \text{ No. 1 wedge rings}$$

Total number of brick $= \dfrac{2\pi 129 \times 17}{2\frac{1}{2} \times 4\frac{1}{2}} = 1{,}230$ nine-inch equivalents in whole dome

$$1{,}230 \times {}^{15}/_{54} = 342 \text{ No. 1 wedges}$$

$$(1{,}230 - 242)^{58}/_{90} = 585 \text{ No. 1 keys}$$

$$1{,}230 - 880 = 303 \text{ straights}$$

Domes can be constructed with 4½-in. rings, which are sometimes favored for movable structures like covers. The calculation can be carried out in the same way. As each ring in the dome is self-supporting, a complete form is not needed.

Steelwork. The dome is particularly easy to brace because a simple tension band around the base will take care of the stresses completely. The section of this band can be easily computed from the formulas previously given, allowing a factor of safety of at least 5 to take care of the elevated temperatures, corrosion, and scaling.

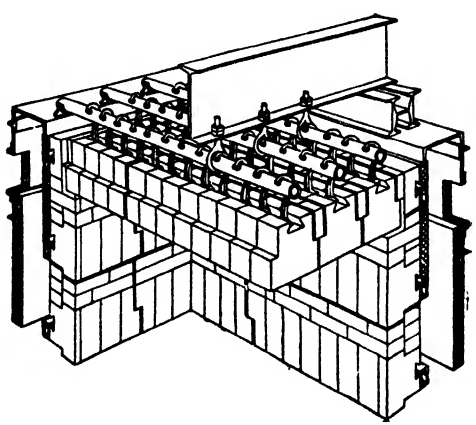


FIG. 418. Typical suspended-arch construction. Reintjes, each tile individually supported and removable. (*Courtesy of Power Magazine.*)

7. Suspended Arches. *Firebrick Suspended Arches.* Suspended arches consist of a type of construction where individual refractory units are held in place by a metal support tied to an overhead framework. In this type of arch, a single unit can be replaced without disturbing the whole crown.

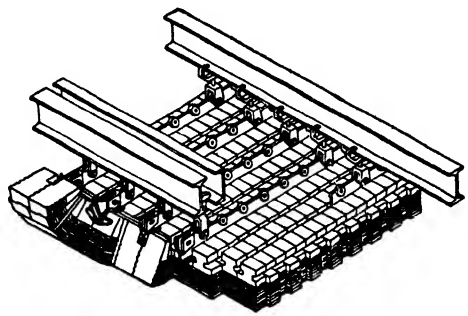


FIG. 418. Detrick tile corrugated on all sides prevent spalled refractory from falling into furnace.

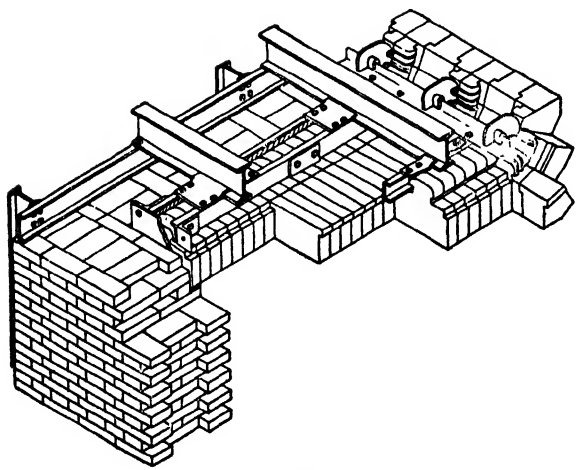


FIG. 418. American arch, alternate rows of tile removable without disturbing channel suspension.

A great many types of block are used for constructing these arches, some of the best known being shown in Figs. 418. This type of construction is useful for flat or special shaped roofs. It also allows an unlimited width. However, it cannot be insulated so completely as the sprung arch and is somewhat more costly.

Some of the basic roofs in German open-hearth furnaces make use of a

combination sprung and suspended arch that seems to have some advantages for this purpose.

Insulating-firebrick Suspended Arches. Insulating firebrick are particularly adapted to use in suspended arches because they are light in weight and thus permit an inexpensive supporting framework. Two typical types

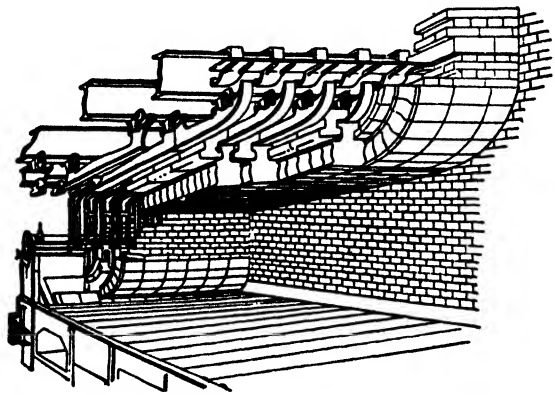


FIG. 418. Bigelow-Liptak, double suspensions increase refractory that can be eroded.

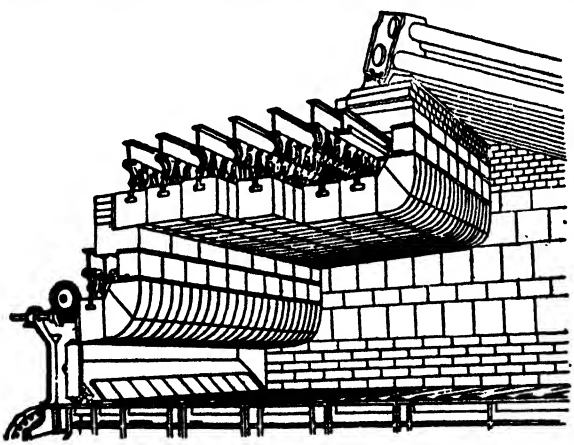


FIG. 418. McLeod & Henry, each tile individually supported and removable.

of suspended arch developed by the Babcock and Wilcox Company are shown in Fig. 419, where the brick units are threaded on light steel or alloy rods and supported on light steel hangers. Such a roof is comparatively inexpensive to set up and generally gives excellent service. This type of construction is used a great deal in the larger heat-treating furnaces and oil stills because there is no limit to the span that can be obtained. It also

finds application in soaking pit covers where the light weight allows rapid action.

In this type of roof, 9-in. straights can be used, which are easy to drill and assemble. The high insulating value of the insulating firebrick keeps the supporting steelwork comparatively cool. Usually the whole roof,

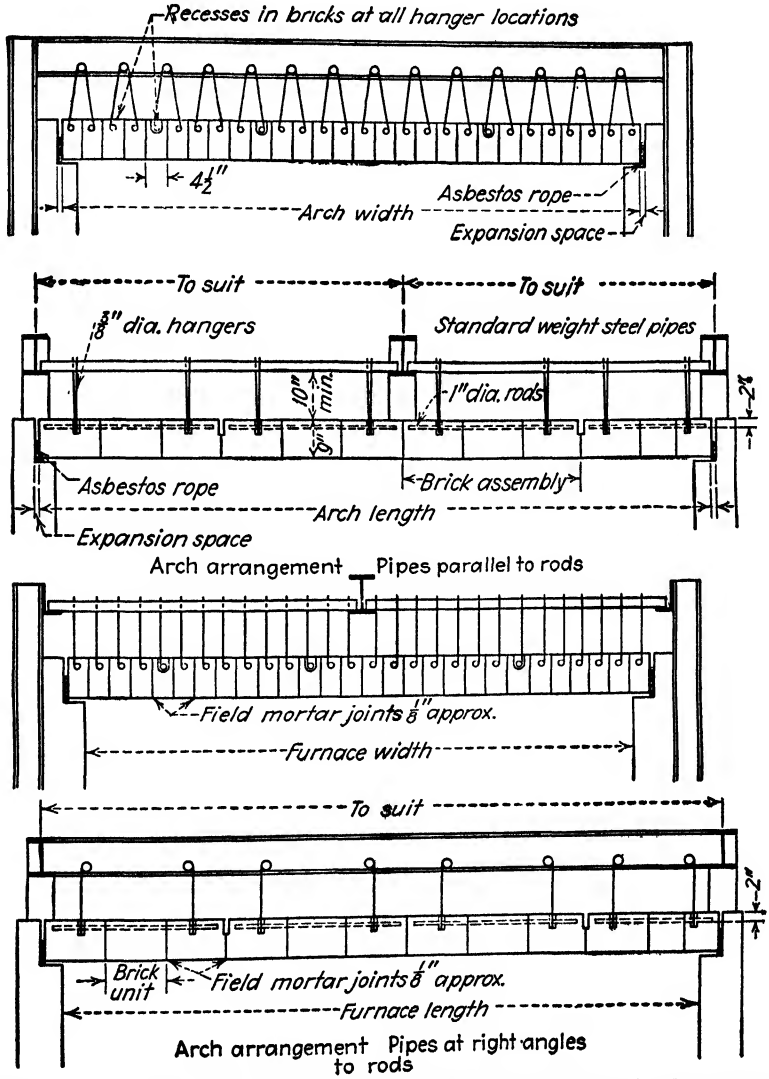


FIG. 419. Arrangement of Babcock & Wilcox insulating firebrick for 9-in. flat suspended arches. (*Courtesy of Babcock and Wilcox Company.*)

TABLE 157. TEMPERATURE EQUIVALENTS OF ORTON PYROMETRIC CONES

Cone No.	End point, 20°C. per hr.		End point, 150°C. per hr.	
	°C.	°F.	°C.	°F.
022	585	1090	605	1120
021	595	1100	615	1140
020	625	1160	650	1200
019	630	1170	660	1220
018	670	1240	720	1330
017	720	1330	770	1420
016	735	1360	795	1460
015	770	1420	805	1480
014	795	1460	830	1530
013	825	1520	860	1580
012	840	1540	875	1610
011	875	1610	905	1660
010	890	1630	895	1640
09	930	1710	930	1710
08	945	1730	950	1740
07	975	1790	990	1810
06	1005	1840	1015	1860
05	1030	1890	1040	1900
04	1050	1920	1060	1940
03	1080	1980	1115	2040
02	1095	2000	1125	2060
01	1110	2030	1145	2090
1	1125	2060	1160	2120
2	1135	2080	1165	2130
3	1145	2090	1170	2140
4	1165	2130	1190	2170
5	1180	2160	1205	2200
6	1190	2170	1230	2250
7	1210	2210	1250	2280
8	1225	2240	1260	2300
9	1250	2280	1285	2350
10	1260	2300	1305	2380
11	1285	2350	1325	2420
12	1310	2390	1335	2440
13	1350	2460	1350	2460
14	1390	2530	1400	2550
15	1410	2570	1435	2620
16	1450	2640	1465	2670
17	1465	2670	1475	2690
18	1485	2710	1490	2710
19	1515	2760	1520	2770
20	1520	2770	1530	2790
23			1580*	2880*
26			1595	2900
27			1605	2920
28			1615	2940
29			1640	2980
30			1650	3000
31			1680	3060
32			1700	3090
33			1745	3170
34	1755	3190	1760	3200
35	1775	3230	1785	3250
36	1810	3290	1810	3290
37	1830	3330	1820	3310
38	1850	3360	1835	3340
39	1865	3390		
40	1885	3430		
41	1970	3580		
42	2015	3660		

*Cones 23 to 38 heated at 100°C. per hr.

TABLE 158. STANDARD CALIBRATION DATA FOR CHROMEL-ALUMEL COUPLES

E.m.f., millivolts	Reference junction at 0°C.					
	0	10	20	30	40	50
	Temperature, 0°C.					
0	0	246	485	720	966	1232
0.2	5	251	490	725	972	1237
.4	10	256	494	730	977	1243
.6	15	261	499	735	982	1249
.8	20	266	504	740	987	1254
1.0	25	271	508	744	992	1260
1.2	30	276	513	749	997	1266
1.4	35	280	518	754	1002	1271
1.6	40	285	523	759	1007	1277
1.8	45	290	527	764	1013	1283
2.0	50	295	532	768	1018	1288
2.2	54	300	537	773	1023	1294
2.4	59	305	541	778	1028	1300
2.6	64	310	546	783	1033	1306
2.8	69	315	551	788	1038	1311
3.0	74	319	555	792	1044	1317
3.2	79	324	560	797	1049	1323
3.4	83	329	565	802	1054	1329
3.6	88	334	570	807	1059	1334
3.8	93	338	574	812	1065	1340
4.0	98	343	579	817	1070	1346
4.2	102	348	584	822	1075	1352
4.4	107	353	588	827	1081	1358
4.6	112	358	593	832	1086	1364
4.8	117	362	598	837	1091	1370
5.0	122	367	602	841	1096	1376
5.2	127	372	607	846	1102	1382
5.4	132	376	612	851	1107	1388
5.6	137	381	616	856	1112	1394
5.8	142	386	621	861	1118	1400
6.0	147	391	626	866	1123	
6.2	152	396	631	871	1128	
6.4	157	400	635	876	1134	
6.6	162	405	640	881	1139	
6.8	167	410	645	886	1144	
7.0	172	414	649	891	1150	
7.2	177	419	654	896	1155	
7.4	182	424	659	901	1161	
7.6	187	429	664	906	1166	
7.8	192	433	668	911	1171	
8.0	197	438	673	916	1177	
8.2	202	443	678	921	1182	
8.4	207	448	683	926	1188	
8.6	212	452	687	931	1193	
8.8	217	457	692	936	1199	
9.0	222	462	697	941	1204	
9.2	227	466	701	946	1210	
9.4	232	471	706	951	1215	
9.6	237	476	711	956	1221	
9.8	241	480	716	961	1226	
10.0	246	485	720	966	1232	

TABLE 159. STANDARD CALIBRATION DATA FOR CHROMEL-ALUMEL COUPLES

E.m.f., millivolts	Reference junction at 32°F.					
	0	10	20	30	40	50
	Temperature, °F.					
0	32	475	905	1329	1772	2250
0.2	41	484	913	1338	1781	2260
0.4	50	493	922	1346	1790	2270
0.6	59	502	930	1355	1799	2280
0.8	68	510	939	1363	1808	2290
1.0	77	519	947	1372	1818	2300
1.2	86	528	956	1380	1827	2310
1.4	95	537	964	1389	1836	2320
1.6	104	546	973	1398	1845	2331
1.8	113	554	981	1407	1855	2341
2.0	121	563	990	1415	1864	2351
2.2	130	572	998	1424	1873	2362
2.4	139	580	1006	1433	1882	2372
2.6	147	589	1015	1441	1892	2382
2.8	156	598	1023	1450	1901	2393
3.0	165	607	1032	1459	1911	2403
3.2	173	615	1040	1467	1920	2413
3.4	182	624	1049	1476	1930	2424
3.6	190	632	1057	1485	1939	2434
3.8	199	641	1065	1494	1949	2445
4.0	208	650	1074	1503	1958	2455
4.2	217	658	1083	1511	1967	2466
4.4	225	667	1091	1520	1977	2476
4.6	234	675	1099	1529	1986	2487
4.8	243	684	1108	1538	1996	2497
5.0	251	693	1116	1547	2005	
5.2	260	701	1125	1555	2015	
5.4	269	710	1133	1564	2024	
5.6	278	718	1142	1573	2034	
5.8	287	727	1150	1582	2044	
6.0	296	735	1158	1591	2053	
6.2	305	744	1167	1600	2063	
6.4	314	752	1175	1609	2072	
6.6	323	760	1184	1618	2082	
6.8	332	769	1193	1627	2092	
7.0	341	778	1201	1636	2101	
7.2	350	786	1210	1645	2111	
7.4	359	795	1218	1654	2121	
7.6	368	803	1227	1663	2130	
7.8	377	812	1235	1672	2140	
8.0	386	820	1243	1680	2150	
8.2	395	829	1252	1689	2160	
8.4	404	838	1260	1698	2170	
8.6	413	846	1269	1708	2180	
8.8	422	855	1278	1717	2190	
9.0	431	863	1286	1726	2200	
9.2	440	872	1295	1735	2210	
9.4	449	880	1303	1744	2220	
9.6	457	889	1312	1753	2230	
9.8	466	897	1320	1762	2240	
10.0	475	905	1329	1772	2250	

TABLE 160. STANDARD CALIBRATION DATA FOR THERMOCOUPLES FROM PLATINUM AND PLATINUM ALLOYED WITH 10 PER CENT RHODIUM

E.m.f., microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000
	Temperatures °C.									
0	0.0	147.1	265.4	374.3	478.1	578.3	675.3	769.5	861.1	950.4
100	17.8	159.7	276.6	384.9	488.3	588.1	684.8	778.8	870.1	959 2
200	34.5	172.1	287.7	395.4	498.4	597.9	694.3	788.0	879.1	968 0
300	50.3	184.3	298.7	405.9	508.5	607.7	703.8	797.2	888.1	976 7
400	65.4	196.3	309.7	416.3	518.6	617.4	713.3	806.4	897.1	985.4
500	80.0	208.1	320.6	426.7	528.6	627.1	722.7	815.6	906.1	994.1
600	94.1	219.7	331.5	437.1	538.6	636.8	732.1	824.7	915.0	1002 8
700	107.8	231.2	342.3	447.4	548.6	646.5	741.5	833.8	923.9	1011.5
800	121.2	242.7	353.0	457.7	558.5	656.1	750.9	842.9	932.8	1020 1
900	134.3	254.1	363.7	467.9	568.4	665.7	760.2	852.0	941.6	1028 7
1,000	147.1	265.4	374.3	478.1	578.3	675.3	769.5	861.1	950.4	1037.3

E.m.f., microvolts	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000
	Temperatures °C.								
0	1037.3	1122.2	1205.9	1289.3	1372.4	1454.8	1537.5	1620.9	1704.3
100	1045.9	1130.6	1214.2	1297.7	1380.7	1463.0	1545.8	1629.2	1712.6
200	1054.4	1139.0	1222.6	1306.0	1389.0	1471.2	1554.1	1637.6	1721.0
300	1062.9	1147.4	1230.9	1314.3	1397.3	1479.4	1562.4	1645.9	1729.3
400	1071.4	1155.8	1239.3	1322.6	1405.6	1487.7	1570.8	1654.3	1737.7
500	1079.9	1164.2	1247.6	1330.9	1413.8	1496.0	1579.1	1662.6	1746.0
600	1088.4	1172.5	1255.9	1339.2	1422.0	1504.3	1587.5	1670.9	1754.3
700	1096.9	1180.9	1264.3	1347.5	1430.2	1512.6	1595.8	1679.3	
800	1105.4	1189.2	1272.6	1355.8	1438.4	1520 9	1604.2	1687.6	
900	1113.8	1197.6	1281.0	1364 1	1446.6	1529.2	1612.5	1696.0	
1,000	1122.2	1205.9	1289.3	1372.4	1454.8	1537.5	1620.9	1704.3	

TABLE 161. STANDARD CALIBRATION DATA FOR THERMOCOUPLES FROM PLATINUM AND PLATINUM ALLOYED WITH 10 PER CENT RHODIUM

E.m.f., microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000
	Temperatures °F.									
0	32.0	296.8	509.7	705.7	892.6	1072.9	1247.5	1417.1	1582.0	1742.7
100	42.0	319.5	529.9	724.8	910.9	1090.6	1264.6	1433.8	1598.2	1758.6
200	94.1	341.8	549.9	743.7	929.1	1108.2	1281.7	1450.4	1614.4	1774.4
300	122.5	363.7	569.7	762.6	947.3	1125.9	1298.8	1467.0	1630.6	1790.1
400	149.7	385.3	589.5	781.3	965.5	1143.3	1315.9	1483.5	1646.8	1805.7
500	176.0	406.6	609.1	800.1	983.5	1160.8	1332.9	1500.1	1663.0	1821.4
600	201.4	427.5	628.7	818.8	1001.5	1178.2	1349.8	1516.5	1679.0	1837.0
700	226.0	448.2	648.1	837.3	1019.5	1195.7	1366.7	1532.8	1694.8	1852.7
800	250.2	468.9	667.4	855.9	1037.3	1213.0	1383.6	1549.2	1711.0	1868.2
900	273.7	489.4	686.7	874.2	1055.1	1230.3	1400.4	1565.6	1726.9	1883.7
1,000	296.8	509.7	705.7	892.6	1072.9	1247.5	1417.1	1582.0	1742.7	1899.1

E.m.f., microvolts	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000
	Temperatures °F.								
0	1899.1	2052.0	2202.6	2352.7	2502.3	2650.6	2799.5	2949.6	3099.7
100	1914.6	2067.1	2217.6	2367.9	2517.3	2665.4	2814.4	2964.6	3114.7
200	1929.9	2082.2	2232.7	2382.8	2532.2	2680.2	2829.4	2979.7	3129.8
300	1945.2	2097.3	2247.6	2397.7	2547.1	2694.9	2844.3	2994.6	3144.7
400	1960.5	2112.4	2262.7	2412.7	2562.1	2709.9	2859.4	3009.7	3159.9
500	1975.8	2127.6	2277.7	2427.6	2576.8	2724.8	2874.4	3024.7	3174.8
600	1991.1	2142.5	2292.6	2442.6	2591.6	2739.7	2889.5	3039.6	3189.7
700	2006.4	2157.6	2307.7	2457.5	2606.4	2754.7	2904.4	3054.7	
800	2021.7	2172.6	2322.7	2472.4	2621.1	2769.6	2919.6	3069.7	
900	2036.8	2187.7	2337.8	2487.4	2635.9	2784.6	2934.5	3084.8	
1,000	2052.0	2202.6	2352.7	2502.3	2650.6	2799.5	2949.6	3099.7	

TABLE 162. STANDARD CALIBRATION DATA FOR COPPER-CONSTANTAN THERMOCOUPLE

E.m.f., microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000
	Temperatures °C.									
0	0.0	25.3	49.2	72.1	94.1	115.3	135.9	155.9	175.5	194.6
100	2.6	27.7	51.5	74.3	96.2	117.4	137.9	157.0	177.4	196.5
200	5.2	30.2	53.9	76.5	98.4	119.5	140.0	159.9	179.4	198.4
300	7.7	32.6	56.2	78.8	100.5	121.6	142.0	161.9	181.3	200.3
400	10.3	35.0	58.5	81.0	102.7	123.6	144.0	163.8	183.2	202.2
500	12.8	37.4	60.8	83.2	104.8	125.7	146.0	165.8	185.1	204.0
600	15.3	39.8	63.0	85.4	106.9	127.7	148.0	167.7	187.0	205.9
700	17.8	42.2	65.3	87.6	109.0	129.8	150.0	169.7	188.0	207.8
800	20.3	44.5	67.6	89.7	111.1	131.8	152.0	171.6	190.8	209.8
900	22.8	46.9	69.8	91.9	113.2	133.9	154.0	173.6	192.7	211.5
1,000	25.3	49.2	72.1	94.1	115.3	135.9	155.9	175.5	194.6	213.4

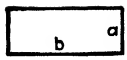
E.m.f., microvolts	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000
	Temperatures °C.								
0	213.4	231.7	249.8	267.6	285.1	302.4	319.5	336.4	353.1
100	215.2	233.6	251.6	269.4	286.9	304.1	321.2	338.0	
200	217.2	235.4	253.4	271.1	288.6	305.9	322.9	339.7	
300	218.9	237.2	255.2	272.9	290.3	307.6	324.6	341.4	
400	220.8	239.0	257.0	274.6	292.1	309.3	326.3	343.1	
500	222.6	240.8	258.7	276.4	293.8	311.0	327.9	344.7	
600	224.4	242.6	260.5	278.2	295.5	312.7	329.6	346.4	
700	226.3	244.4	262.3	279.9	297.3	314.4	331.3	348.1	
800	228.1	246.2	264.1	281.6	299.0	316.1	333.0	349.7	
900	229.9	248.0	265.8	283.4	300.7	317.8	334.7	351.4	
1,000	231.7	249.8	267.6	285.1	302.4	319.5	336.4	353.1	

TABLE 163. STANDARD CALIBRATION DATA FOR COPPER-CONSTANTAN THERMOCOUPLE

E.m.f., microvolts	0	1,000	2,000	3,000	4,000	5,000	6,000	7,000	8,000	9,000
	Temperatures °F.									
0	32.0	77.5	120.6	161.7	201.3	239.6	276.6	312.7	347.9	382.3
100	36.7	81.9	124.8	165.7	205.2	243.3	280.3	314.6	351.4	385.7
200	41.4	86.3	128.9	169.8	209.1	247.1	283.9	319.8	354.8	389.1
300	45.9	90.6	133.1	173.9	212.9	250.8	287.6	323.3	358.3	392.5
400	50.5	95.0	137.2	177.7	216.8	254.5	291.2	326.9	361.8	395.9
500	55.0	99.3	141.4	181.7	220.6	258.2	294.8	330.4	365.2	399.3
600	59.5	103.6	145.5	185.7	224.4	261.9	298.4	333.9	368.6	402 6
700	64.0	107.9	149.5	189.6	228.2	265.6	302.0	337.4	370.4	406.0
800	68.5	112.1	153.6	193.5	232.0	269.3	305.6	340.9	375.6	409.3
900	73.0	116.3	157.7	197.4	235.8	273.0	309.1	344.4	378.9	412.7
1,000	77.5	120.6	161.7	201.3	239.6	276.6	312.7	347.9	382.3	416.0

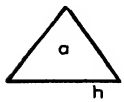
E.m.f, microvolts	10,000	11,000	12,000	13,000	14,000	15,000	16,000	17,000	18,000	19,000
	Temperatures °F.									
0	416.0	449.1	481.7	513.7	545.2	576.4	607.1	637.4	667.6	
100	419.4	452.4	484.9	516.8	548.4	579.4	610.1	640.5		
200	423.0	455.7	488.1	519.0	551.5	582.5	613.2	643.5		
300	426.0	459.0	491.3	523.2	554.6	585.6	616.2	646.5		
400	429.3	462.2	494.5	526.4	557.7	588.7	619.3	649.5		
500	432.7	465.5	497.7	529.5	560.8	591.8	622.3	652.5		
600	436.0	468.7	500.9	532.7	564.0	594.8	625.4	655.5		
700	439.3	472.0	504.1	535.8	567.1	597.9	628.4	658.5		
800	442.6	475.2	507.3	539.0	570.2	601.0	631.4	661.6		
900	445.9	478.4	510.5	542.1	573.6	604.0	634.4	664.6		
1,000	449.1	481.7	513.7	545.2	576.4	607.1	637.4	667.6		

TABLE 164. FORMULAS USEFUL IN CALCULATIONS



Rectangle:

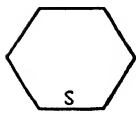
$$\text{Area} = ab$$



Triangle:

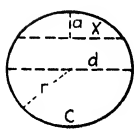
$$\text{Area} = \frac{ah}{2}$$

Regular Polygon:



Sides	Area
5	$1\ 720 \times S^2$
6	$2\ 598 \times S^2$
7	$3\ 634 \times S^2$
8	$4.828 \times S^2$
9	$6.182 \times S^2$
10	$7.694 \times S^2$
11	$9.366 \times S^2$
12	$11.196 \times S^2$

Circle:



Circumference $= \pi d = 2\pi r$

Diameter $= 2r = \dfrac{C}{\pi} = 2\sqrt{\dfrac{\text{area}}{\pi}}$

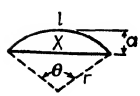
Radius $= \dfrac{d}{2} = \dfrac{C}{2\pi} = \sqrt{\dfrac{\text{area}}{\pi}}$

Area $= \dfrac{\pi d^2}{4} = \pi r^2 = 0.7854d^2$

Length of chord, $x = 2\sqrt{a(d-a)^2} = 2r(\sin \tfrac{1}{2}\theta)$

Segment:

$$\text{Area} = \frac{rl - x(r-a)}{2}$$

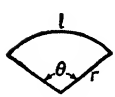


Height of arc above chord, $a = r - \sqrt{r^2 - (x/2)^2}$

Radius, when chord and height are known, $r = \dfrac{(x/2)^2 + h^2}{2h}$

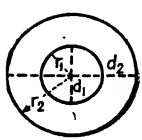
Length of arc, $l = 2\pi r \dfrac{\theta}{360} = \pi r \dfrac{\theta}{180}$

Sector:

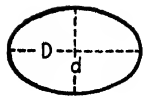


$$\text{Area} = \frac{1}{2}lr = \pi r^2 \frac{\theta}{360}$$

Annulus (Circular Ring):



$$\text{Area} = \pi(r_2^2 - r_1^2)$$
$$= \pi(r_2 + r_1)(r_2 - r_1)$$
$$= 0.7854(d_2^2 - d_1^2)$$



Ellipse:

$$\text{Area} = \frac{\pi}{4} Dd = 0.7854Dd$$

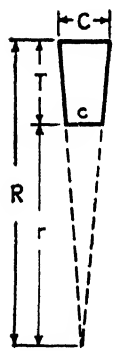
$$\text{Perimeter (approx.)} = 2\pi \sqrt{\frac{D^2 + d^2}{8}}$$

Skewbacks:

To find a skew to fit a given arch:

1. Find subtended angle θ
2. Find sine and cosine of $\frac{1}{2}\theta$
3. H = thickness of arch $\times$ sin $\frac{1}{2}\theta$
4. V = thickness of arch $\times$ cos $\frac{1}{2}\theta$

Slope of the skewback from the horizontal = $90° - \frac{1}{2}\theta$



Circle Brick:

Radius of radial brick, r $\quad \dfrac{cT}{(C - c)}$

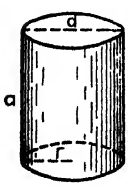
Number of radial brick to make a circle:

$$n = \frac{\pi \times \text{diameter of circle}}{\text{thickness of large end}}$$

$$= \frac{2\pi r}{C}$$

Number of straights to fill out a circle of given diameter using given number of radial brick:

$$n = \frac{\pi(\text{given outside diameter}) - (\text{possible diameter with radial brick})}{\text{thickness of straight}}$$



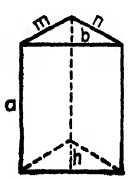
Cylinder:

Volume $= \pi r^2 a$

$= 0.7854\, d^2 a$

Cylindrical surface area $\quad \pi\, da$

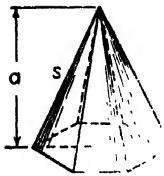
Total surface area $\quad 2\pi r(r + a)$



Regular Triangular Prisms:

Volume $= \frac{1}{2}bha$

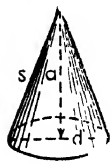
Lateral surface area $= (b + m + n)a$



Pyramid:

$$\text{Volume} = \frac{\text{area of base} \times a}{3}$$

$$\text{Lateral surface area} = \frac{\text{perimeter of base} \times s}{2}$$

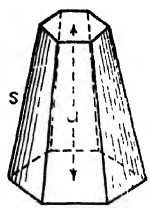


Cone:

$$= 0.2618\, d^2 a$$

$$\text{Lateral surface area} = \pi r s$$

Frustum of Pyramid:

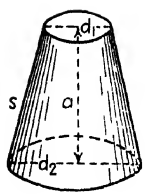


$$\text{Lateral surface area} = \frac{(P + p)s}{2}$$

$$\text{Volume} = \frac{a}{3}(b + B + \sqrt{Bb})$$

where P = perimeter of lower base
p = perimeter of upper base
B = area of lower base
b = area of upper base

Frustum of Cone:

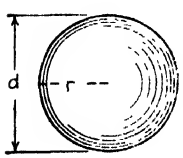


$$\text{Volume} = \frac{a}{3}(b + B + \sqrt{Bb}), \text{ or}$$

$$= \frac{\pi}{12} a(d_1^2 + d_1 d_2 + d_2^2)$$

$$\text{Area of conic surface} = \frac{\pi S}{2}(d_1 + d_2)$$

Sphere:

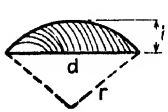


Area of surface $4\pi r^2 = \pi d^2$ $12.5664\, r^2$

Volume $\frac{4\pi r^3}{3}$ $4.1888 r^3$

$\frac{\pi d^3}{6} = 0.5236 d^3$

Segment of Sphere:



$$\text{Area of spherical surface} = 2\pi r h = \frac{\pi}{4}(d^2 + 4h^2)$$

$$\text{Volume} \quad \pi h^2 \left(r - \frac{h}{3}\right)$$

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